

NON-EQUILIBRIUM POSITIVE DIFFUSION AS NEARBY TO
MICROSCOPIC SCALE

By

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NON-EQUILIBRIUM CARRIER TRANSPORT OF ELECTROLYTES IN
MEMBRANE DEVICES

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In modeling membrane-mediated transport, a-coupling is often simplified by assuming instantaneous equilibrium between transport and reaction-desorption steps. Some exhibiting behavior that deviates from that predicted by this simple model have been reported, challenging the validity of these assumptions. This modified reaction behavior has been attributed to several different factors, including kinetic reaction reversibility, diffusion rate transfer resistance, ion-ion coupling, and reaction-desorption non-equilibrium. These factors are analyzed and their relative impact on membrane transport is evaluated. For hydrophobic organic compounds, physical non-equilibrium (i.e., rate-limited mass transfer to aggregated or trapped systems) and ion-ion coupling (rate-limited diffusion within the polymer matrix) are probably the predominant factors causing non-equilibrium. The relative importance of these factors is media-dependent. For smaller ionic systems, more

transfer limitations associated with aggregated media and/or various organic matter appear to predominate. Various spatial heterogeneity aspects to be discussed at the Symposium.

Experimental methods for investigating the reaction kinetics of organic substrates were developed and evaluated. These methods were employed to investigate the reactions involved in nonequilibrium respiration. A long-term linear relationship was observed between the kinetic respiration constant and the equilibrium respiration constant, this relationship was quantified. The influence of various substrate effects on reaction kinetics was recognized. The influence of organic substrate on the nonequilibrium respiration of organic substrates was investigated; experiments revealed that the kinetic respiration constant is logarithmically correlated to the fraction of substrate. A model explaining the influence of organic substrate on reaction kinetics was developed. A model for simulating solute transport under conditions of substrate sources of nonequilibrium was developed and evaluated. A model simulating solute transport at the field scale, where combining my results from several previous, was developed.

CHAPTER 1 INTRODUCTION

Before Transport

With increasing interest over groundwater contamination, research on subsurface transport and flow, subsurface transport modeling, and groundwater remediation technology has grown rapidly. Knowledge of the various physical, chemical, and biological processes that affect groundwater contaminants is essential for such research. Of the various processes, sorption is one of the most important. In our book previous efforts on subsurface transport (flow, and transport).

Investigation of sorption sensitivity is a relatively new and multi-disciplinary endeavor. A large body of literature is developing, with contributions from chemical engineering, petroleum engineering, analytical chemistry, environmental engineering, and civil engineering. In addition to well releases and groundwater geology/hydrology.

The conventional equation used to describe adsorption-desorption, one-dimensional steady-state transport of a sorbing solute in (liquid and immobile, (SVE)

$$\frac{dC}{dx} + \frac{dS}{dx} = 0 \quad \left(\frac{dC}{dx} \right) = -v \frac{dS}{dx} \quad (1-1)$$

where C is solution-phase solute concentration (M^3/L^3), S is sorbed-phase solute concentration (M^3/L^3), D is dispersion coefficient (L^2/T), v is average groundwater velocity (L/T), ρ is bulk density (M/L^3), θ is water volume content (L^3/L^3), x is distance (L) and t is time (T). Assuming

the h_1/h_2 term is often the critical step in model formulation. The typical approach has been to assume that conditions of local equilibrium, isochoric singularity, and isochoric flow rate exist. This assumption greatly simplifies the resultant expression for h_1/h_2 which is $R_p \cdot h_1/h_2$. Upon substitution, the transport equation becomes

$$1 \frac{dC}{dt} = 1 \frac{dC_p}{dt} = \tau \frac{dC}{dt} \quad (1-3)$$

where $1 = (1 + C_p/R_p) \cdot R_p$ is the retardation factor (R_p = equilibrium sorption constant). This equation will hereafter be referred to as the advective-dispersive (A/D) transport equation.

Equation (1-3) may be written in the following non-dimensional form

$$1 \frac{dC^*}{dP} = 1 \frac{dC_p^*}{dP} = \frac{C_p^*}{P} \quad (1-4)$$

by introducing the following dimensionless parameters

$$C^* = \frac{C}{C_0} \quad P = \frac{2L}{R} \\ P = \frac{2L}{R} \quad R = \frac{R}{L}$$

The factor number (P) describes the slope of the solute breakthrough curve ($1 =$, magnitude of dispersion) and R describes the partition (relative to the mean velocity of water). The solution to equation (1-4) under Dan-type boundary conditions is given by Brauer (1970) for various P values and with $R=1$. Inspection of model output shows that, as P increases, the breakthrough curve (BTC) approaches a symmetrical, sigmoidal shape. However, for P less than approximately 10, the BTC is noticeably asymmetrical. This asymmetry is the result of a very large dispersive-transport component ($1 =$ large R).

The assumptions employed to derive eq. 1-1 simplify transport analysis and may be adequate under certain conditions. Some exhibiting behavior that deviates from that predicted by the single model have been reported, however, challenging the validity of this approach. This method requires behavior has been attributed to several different factors, including bimodal sorption reactions, diffusion rate transfer mechanisms, interface nonlinearity, and sorption-desorption non-equilibrium.

More use of more of the conditions that were assumed to derive eq. 1-1 are not met, the 1-1 model will not fully describe solute-transport data. In these situations, the data may be characterized as exhibiting nonlinearity. As a majority of the past and present groundwater investigations involving effluents have employed the 1-1 model and its associated assumptions, it is important to analyze the validity of this approach. For cases where the 1-1 model is not valid, the effects of nonlinearity on groundwater contaminant transport, modeling, and remediation need to be assessed.

Transport Nonlinearity in Structural Cells and Spillars

The literature is replete with reports on the influence of cell structure on solute transport. Such reports date back to over 100 years ago (Helmreich, 1844; Lewis et al., 1892), as noted by Hahn (1991). The explanation that the observed nonlinear behavior (e.g., "preferential flow," "anomalous flow," "channeling," "short-circuiting," "bypassing," "partial displacement," "nonuniform stress flow") is the result of non-uniform pore-size distributions (i.e., non-uniform velocity field) is

generally accepted. To model such systems a bimolecular approach (Hessman and Rao, 1984) is often employed. With this approach the porous medium is considered to be composed of two domains: a "mobile" domain, where solute transport occurs by advection and dispersion, and an "immobile" domain, in which there is solute adsorption (flow). The mobile-immobile conceptualization for wells dates back at least 20 years, when it was used by Taylor and Raman (1964). Early mathematical models employing this conceptualization were presented by Neuge and Haverkamp (1984) and van Duin et al. (1979).

Rapid transport in the mobile domain is accompanied by significant mass transfer of solutes between the mobile and immobile domains, which results in the latter behaving as sink/source components. Solute transport in such systems, as described by breakthrough curves (BTCs), is characterized by early tailed breakthrough and by "tailing" or delayed approach to relative concentration values of 0 or 1. Because much of the porous medium is constrained by diffusive mass transfer, solute in the system may be considered to be in a state of nonequilibrium. This phenomenon has been termed physical or transport nonequilibrium (TNE). One of the first to suggest that "dead water" could cause delayed BTCs was Bandrup (1955).

Behavior attributable to TNE has been observed in aggregated heterogeneous (with respect to hydraulic conductivity) and fractured porous media as well as in nonporous media. Some of the earliest work on solute transport in aggregated media, where the nonideality observed in experimentally derived BTCs was attributed to TNE, was performed by Hogg and Hoggan (1964) for nonbinding solutes (N) by Hogg and

Radwan (1961) for sorbing inorganic solutes (Hg^{2+}) and by Kirick et al. (1966), Ray and Kirick (1967), Radwan et al. (1968), Davidson and Gung (1970) and Hsieh et al. (1968, 1971) for organic compounds (quartzite residues, lindane, dieldrin, and picloram). These experiments were all performed with packed soil columns, and while demonstrating the influence of soil aggregation on solute transport they are not completely representative of field conditions. In an attempt to more closely simulate field conditions, chloride displacement studies have been performed using undisturbed soil cores. Early experiments of this nature demonstrating residual solute transport of Cl^- which was attributed to micropore flow, were reported by Kirick and French (1964). Numerous studies of a similar nature have since been reported for Cl^- and other nonreacting solutes (see Hsieh, 1981; Jones and Jermolov, 1981). Similar work has been reported, although to a much lesser extent, for sorbing inorganic solutes (e.g., Bradworth, 1981; Javien et al., 1980) and organic solutes (Shin et al., 1980; Bradworth et al., 1987).

Several field studies of solute transport under controlled conditions, where transport mechanisms was attributed to DR, have been performed for inorganic (e.g., Indaresmanian et al., 1981; Wild and Bolter, 1984). An early study of DR in field-scale transport of an organic solute (quartzite picloram) was performed by Ray et al. (1976). Other studies for organics (Jones and Shin, 1980; Jary et al., 1986a) have since been reported.

The Macmillan concept may also be applied to heterogeneous porous media, such as systems consisting of lenses of varying hydraulic

mobile/immobile (3). In this case, the high-E layer(s) correspond(s) to the "mobile zone" and the low-E layer(s) to the "immobile zone". Solute transport is affected by mass transfer between the high- and low-E layers. The mass transfer mechanism may be explained as follows: solute adsorption is greater in the high-E than in the low-E layers, and as a result, differential solute-front advancement occurs in the different layers, which creates lower-layer concentration gradients. Hence, lower-layer diffusion solute transfer occurs, which results in TPE. A diffusion-based model of this type was presented by Gillham et al. (1984), while Davis and Goltz (1985) applied a mass-transfer-based model to data obtained from a sorption-gradient field experiment. Transport in fractured media can also be modeled with a bi-mechanism approach. The fractures serve as zones of preferential transport, with the total-fracture matrix acting as a diffusional sink/source component (e.g., Gelwick and Pflaum, 1988; Levens et al., 1988).

Several mechanisms are involved in the solute-transfer process in a system representative of the mobile-immobile concept: (1) advective-dispersive transport from bulk solution to the boundary layer (i.e., adsorbed water surrounding the surface), (2) diffusive transport across the adsorbed water (i.e., film diffusion), and (3) pore and/or surface diffusion within the liquid/solid regions (i.e., lattice-aggregate diffusion). Any or all of these three components may be a rate-limiting step. To simplify, it is usually assumed that one of the three steps is slow relative to the other two and may therefore be designated as the primary rate-limiting step.

The effective-flow domain is generally assumed to be well mixed, thus minimizing the importance of mass transfer resistance within these regions. It appears that film diffusion controls the solute uptake into initially quiescent and dilute, 10% Barrow and Smith, 1971; Han, 1973; Weiss and Liu, 1980; Riley et al., 1981). However, lower aggregate diffusion appears to control solute uptake for the majority of the incubation period (Landauer and Shanks, 1971; Barrow and Smith, 1973; Han, 1973; Barrow, 1980; Chinnenden et al., 1980; Riley et al., 1981; Roberts et al., 1982). Interaggregate diffusion, therefore, is usually the transfer process designated as the rate-limiting step. Here that step is at the surface-liquid interface is assumed to be instantaneous, the rate at which the solute is transported to and from this interface controls the attainment of equilibrium.

Roberts et al. (1982) used the models developed by Chinnenden et al. (1980) to assess the relative contribution of various mass transfer processes to the spreading of the MZ. They analyzed the data of Smith-Clark et al. (1981) for $^3\text{H}_2\text{O}$, Cl^- and Na^+ transport to predict values of an aggregated MZ. Roberts et al. (1982) concluded that the contribution of internal mass transfer resistance to dispersion was three to ten times greater than that of external mass transfer resistance. This greater relative significance of internal mass transfer resistance was also shown by a model sensitivity analysis. The relative importance of internal and external mass transfer resistance was also evaluated by Smith (1982), who found the influence of external mass transfer to be three orders-of-magnitude less than that of internal resistance.

It is important to note that the phenomena attributed to TBE are exhibited by sorption, as well as sorbing, solutes. This highlights the point that the mechanism responsible for this nonequilibrium is a transport component, and that the sorption reaction itself is not involved. If the definition of sorption is limited to the processes occurring at the solid-liquid interface, it is hard to label this case as nonequilibrium transport as does flow.

Solute Displacement under unsteady-state conditions

The displacement presented above has involved systems at or near equilibrium conditions. Phenomena similar to those discussed above have also been observed in unsteady-state systems. Biggar and Nielsen (1962) performed solute displacement studies under unsteady-state conditions and observed "progressive shifting of the BE to the left" as equilibrium was approached. This behavior was attributed to a condition of "stable state" upon desorption. Similar results have since been reported by several researchers.

The influence of unsteady conditions upon solute-transport coefficient (α_s), as measured experimentally, is dependent upon the pore-size distribution of the porous medium. Two general cases can be described as follows:

Uniform distribution. Retardation will generally decrease when equilibrium is reached from sorption for a medium that has a relatively narrow, uniform distribution. ETC obtained under unsteady conditions will exhibit a relatively small amount of dispersive broadening of the uniform distribution. Upon desorption, some fraction of the pores no longer readily transmit water. These pores then become

"lethal" doses that will be distributed (diffused) with respect to components for intake. FGA obtained under unrestricted conditions will exhibit a greater degree of dispersion and may be shifted to the right in comparison to the FGA obtained under restriction because of the impact of the lethal doses. Such behavior shows conditionally responses as well-order stimuli to reduced from restriction. This have reported by several researchers (e.g., Kipper and Wallace, 1968; Kipper and Kirsh 1968; Kirsh et al., 1977; Schmidt and Wierwoge, 1981).

Partial restriction in will-water contact can result in the effective II is, nonselective pre- and distribution more again having uniform and uniform. Relative transport will thus become less uniform, in comparison to that observed for the larger will-water contacts. Relative transport conditionally thus, with limit behavior as will-water contact is reduced from restriction reach a maximum at some critical value of will-water contact that is a function of the willow, and then decreases as will-water contact is further reduced. Such behavior was reported by Kipper and Kirsh (1968) and is exhibited by the data of Schmidt and Wierwoge (1981).

Uniform distribution Relative transport under restricted conditions in porous media characterized by a wide pore size distribution (e.g., porous of transport) will exhibit uniform behavior, as discussed above. The transport data upon distribution which results in a narrowing of the effective pre- and distribution. Relative transport conditionally will thus be reduced when will-water contact is reduced from restriction. Such behavior has been observed, for example, by Kirsh and French (1968) and Saphir and Rao (1981).

It is likely that once the largest pores are desolved, the porous medium will thereafter exhibit behavior similar to that discussed in case (1). Further reduction in solid-phase content will create immobile regions and should be accompanied increasingly after the critical solid-phase content is reached. Further reduction will eliminate the immobile regions, resulting in a reduction in nonideality.

Modeling transport-related nonequilibrium

Solute transfer between the mobile and immobile regions can be accounted for in three ways:

1. explicitly, with the use of Fick's law to describe the physical mechanism of diffusive transfer;
2. explicitly, with the use of an explicit, first-order mass-transfer expression, in place of the mechanistic expression of (1), to approximate solute transfer; and
3. implicitly, with the use of an effective or lumped dispersion coefficient that includes the effects of adsorption, diffusion, as well as hydrodynamic dispersion and axial diffusion. This lumped parameter replaces the usual hydrodynamic dispersion coefficient (D) in the advection-dispersive transport equation. These three approaches will be discussed below.

Physical diffusion models: Early development of the physical diffusion model took place in the chemical engineering field (e.g., Hinchey and Smith, 1960; Kohn et al., 1974; Jones, 1983; Pellerin, 1984). But not as widely applied these models to describe nonequilibrium in soils (Kas et al., 1986a; Lee et al., 1986b; Hsu-

Kinn et al. (1992). Wu and Fedorow (1994) extended this approach to study the complex kinetics of organic solutes.

The above models assume that the film-transfer resistance is negligible. If this is not the case, inclusion of a film-transfer parameter could improve model accuracy. Such a two-resistance model was presented by Sideridou et al. (1994) and Miller and Weber (1998). Solute transfer from mobile to immobile regions is described by a sorption control diffusion through a boundary layer surrounding the particle. It is film transfer followed by diffusion within the aggregate.

The diffusion-based models discussed above were developed assuming a spherical geometry. A conceptually similar model, employing a cylindrical geometry was presented by van Duinbeek et al. (1994) to describe solute transport in nonporous soil.

The increased accuracy obtained by including the actual solute transfer mechanism in the 2-D model is countered by a corresponding increase in model complexity. To develop the diffusion equation, a geometric description of the porous medium is required. Most models have assumed, primarily for mathematical simplicity, a spherical, uniformly sized aggregate structure. Realistic porous media, however, may be far from this idealization. For the above models to be applicable to more than just a few ideal cases, aggregate size distributions and variations in aggregate shape may be accounted for. In an attempt to apply the simplified model to natural cases, Rao et al. (1991) assumed changing solute diffusion from non-spherical aggregates could be approximated by diffusion from equivalent spheres. They showed that

non-spherical aggregates could be represented by equivalent spherical aggregates whose radii are such that the sphere volume is equal to the volume of the non-spherical aggregate. Hansen extended a physical diffusion model developed for spherical aggregates (1941) to spherular and cylindrical shapes (1946a). A form factor was employed to adjust the latex-particle diffusion equation to the selected shape. It was shown that wet aggregate shape could be approximated with neither by employing the area ratio of wetted aggregate surface area to total wet periphery. The approximations gave nearly identical RRs for short and long contact times, and relatively minor deviations for intermediate times.

A method that extends the physical diffusion model to more general conditions involving aggregates with non-spherical geometries has been developed by van den Hulst (1952). The method is based on the use of a geometry-dependent shape factor (β) that can be used to transform an aggregate of a given shape and size into an equivalent sphere with similar diffusion characteristics as the original aggregate. While the shape transformation was found to be accurate, it is limited to uniformly sized aggregates, and no provisions are given to deal with clusters of aggregate sizes. The effect of various aggregate shapes on coagulation was assessed by Hansen (1946a). For early times, coagulation rates were nearly identical for spherical, spherulized, and spherular aggregates. For longer times, the rates were less greatest for the spherular and lowest for the spherulized aggregation. The spherular and cylindrical aggregates have coagulation rates greater than the spherical because, for equivalent characteristic lengths ($\lambda = r$), equal

volume) the surface-to-volume ratios of disks and cylinders are greater than that of a sphere's 1.5, 1.7, and 4.8, respectively) as a result of positive uptake rates, a delay in volume breakthrough (i.e., reduced early breakthrough) and a reduction in tailing would be expected for cylindrical and slabular aggregate systems.

To extend the physical diffusion model to actual field situations, aggregate-size distributions (ASD)—as well as aggregate-shape variations, must be detailed. A method whereby a range of spherical aggregate sizes can be reduced to a single equivalent aggregate size described by Rao et al. (1982). The method involves computing the equivalent radius from the volume-weighted radii of each aggregate-size class. It was shown that the equivalent aggregate could provide a good approximation of diffusion in the actual sized aggregate-size medium. The validity of this approach was further validated by Ward-Clute et al. (1985), where a distribution of aggregate sizes (0.5 to 8.0 μ m in diameter) and shapes was well represented by an equivalent spherical aggregate. Several forms of an aggregate-size-distribution weighting factor were derived by Tracy (1984).

Involving the shape transformations of van den Hulst (1955) or Rosin-Rammler (1934) with the aggregate size-distribution transformation of Tracy (1984) or Rao et al. (1982), a porous medium consisting of different sizes of aggregate having various nonspherical shapes can be transformed into a representative medium consisting of an equivalent, spherical aggregate of an equivalent medium size. In this manner, the physical diffusion model may be extended to any real-world, field situation.

Aggregate-size distribution (ASD) was directly taken into account in a model proposed by Sahasr et al. (1986a). The effect of ASD was modeled by assuming a progressively swelling hypothetical aggregate representative of the actual system at any time. This progressively swelling representative aggregate is, in effect, an effective characteristic aggregate whose size increases with time. The size of the effective aggregate is time-dependent because of differential volume uptake rates for different-sized aggregates. In early times, smaller aggregate domains uptake, therefore, the effective aggregate is small. As time increases, the larger aggregates become more important, which results in an increase in the effective aggregate size. The effective aggregate reaches a maximum size as sorption approaches equilibrium. The Sahasr model describes the ASD from the diffusion equation relation. Knowledge of the size-distribution function or of the average aggregate size is not required. It is not possible, however, to derive an absolute value for the inter-particle diffusion coefficient.

A model that directly includes in the transport equation provisions for an aggregate-size distribution has been developed by Bismann (1990). Any discrete distribution is allowed, and the following parameters: aggregate shape, lattice-aggregate diffusion coefficient, film mass-transfer coefficient, and sorption equilibrium constant may vary for each size class. The size distribution is accounted for by the employment of the parameter $F(b)_i$, the volume fraction of aggregate size-class i with radius b ($i = 1, \dots$, the ratio of the total volume of aggregate size-class i to the total aggregate volume). In effect, the influence of each size class on solute transport is weighted by the

relative properties of the total distribution. Goring et al. (1981) found 26 to be the minimum required number of aggregate-size classes to obtain accurate results. This model, in a very simple manner, allows aggregate-size distributions and aggregate-shape variations to be included directly into solute-transport equations. The applicability and ease of use of the physical diffusion model is thereby greatly enhanced.

The effect of aggregate-size distribution on solute transport has been examined by Roberts et al. (1986) and Hansen (1986). All was observed to delay solute breakthrough and to increase the time required to reach complete breakthrough ($C/C_0 = 1$). The latter effect is slight, whereas the former is major. Breakthrough delay ($C/C_0 < 1$; reduced early breakthrough) is a result of the increased number of smaller-size aggregate-size classes. These smaller aggregates have a greater total external surface area. This results in an inflated area of solute uptake greater than average, which results in a delayed breakthrough. Increased tailing is a result of an increased number of larger-size aggregate-size classes. Because of their increased individual volume and reduced surface-to-volume ratios, these aggregates approach equilibrium more slowly than the average. Therefore, complete breakthrough is delayed. The AD effect on transport was shown to be of greater importance for small lengths, significant size mass transfer rate-dominant distributions, and adsorption toward smaller aggregates (Roberts et al., 1986; Hansen, 1986).

The AD effect is another mechanism that may produce the AD tailing effect. Given the above AD effects, the relevance of an AD

then mass transfer would result in the physical nonequilibrium model, under-structuring tailing and over-structuring early breakthrough. The effects of MS may be ignored (i.e., the porous medium may be treated as an assemblage of well-mixed vessels) when the pore distribution is sufficiently narrow. Ruthven and Burgess (1971) determined mass-transfer deviation $> 15\%$ as being sufficiently narrow. Gossup et al. (1981) found an MS range of less than 10% need to be sufficiently narrow. It should be noted that Harker's model may also be used for cases of aggregates having different sorption properties. For example, systems with different isotherm/diffusion coefficients or different sorption reaction rates may be modeled.

Physical nonequilibrium. Incorporating the uncertainty surrounding pore geometry analysis, the diffusion model may be simplified by replacing the mechanistic description of diffusive transfer with a kinetic first-order mass transfer expression. Kinetic description of the porous medium's structure is then no longer required. Solute transfer is described by a mass transfer coefficient and is assumed to be a function of the solute concentration difference between the mobile and immobile regions. An average immobile-region concentration is also assumed (i.e., a perfectly mixed region). This assumption is in contrast to the physical diffusion model, where concentration gradients within the immobile regions are allowed.

Early development of the physical mass-transfer (or "two-region") model took place in the field of petroleum engineering, where models for two-phase columns were presented by Dean (1961) and Gossup and Smith (1964). The model was extended to sorbing solutes by van Deemter and

Marangoni (1944). This model is, in essence, the linear driving force approximation employed in chemical engineering to simplify the problem of diffusion into spherical particles. This approximation was first suggested by Fick (1855) and later (1947).

Though the transformation techniques mentioned previously (see Gundersen (1989)) are able to quantify the mass-transfer coefficient K_{eff} for the mass-transfer coefficient in terms of physical diffusion model parameters have also been presented by Raman (1981, 1984), and Parker and Valocchi (1984). With the use of the above relationships, the otherwise empirical mass-transfer coefficient can now be expressed in terms of measurable physical parameters. This allows the possibility of independent determination of values for this parameter. In this manner, a major limitation of the physical mass transfer model (parameters obtainable only through curve fitting) may be eliminated.

Effective dispersion model. The third physical nonequilibrium model employs a lumped or effective dispersion coefficient in the conventional $A-B$ transport model. This effective dispersion coefficient implicitly accounts for any diffusive transfer between mobile and immobile regions. Early work in soil science employing this approach was presented by van Duyn (1971) and Parlange and Jury (1971).

As nonequilibrium conditions are approached, the symmetry of a BTC will increase to a point where asymmetry is difficult to discern. Nonequilibrium will then be evidenced only by the increased dispersion. The effective dispersion model will fit experimental data especially well in this case (e.g., Hunt-Blair et al., 1982; Lee et al., 1984).

Comparison of the physical and diffusion models

The above physical models provide a range in complexity and conceptual clarity. It has been shown that both the physical mass-transfer and the effective dispersion models are degenerate cases of the physical diffusion model (Baker, 1991). These approximations will be valid under certain conditions. Hence, the choice of which model to use is dependent upon the nature of conditions, and upon the accuracy provided in relation to their relative simplicity.

The performance of the diffusion and mass-transfer models have been compared by Liu et al. (1988a), Baker (1988), Baker and Roberts (1989), and Miller and Weber (1988). In all four cases, the diffusion model gave results at only slightly better results. Yen and Chaudhari (1980) assessed the ability of the physical mass-transfer model to approximate solutions given by the physical diffusion model. 1000 profiles by the two models for different values of the dimensionless mass-transfer coefficient were compared. The mass-transfer model gave good approximations when values of the dimensionless mass-transfer coefficient were greater than 10. The physical mass-transfer model appeared to give results virtually identical to a physical diffusion model when the following condition was met (Baker and Tolmach, 1980)

$$(D_p/L^2/K_m) > 0.1$$

where D_p is intra-aggregate diffusion coefficient, L is length of lacunae, w is average pore-water velocity, K_m is intra-aggregate retardation factor, and k is aggregate radius. Raghoebar and Roberts (1989) found that the mass-transfer model gave good approximations of the diffusion model for $(D_p/L^2) > 0.1$.

From the foregoing, it appears that the increase in conceptual economy gained with the diffusion model may not justify the additional mathematical complexity and increased number of parameters associated with the model. Hence, the physical mass-transfer model may be preferable as a basis for the model described above.

Interaggregate model

Models of the above type have been unable to completely describe the extensive tailing exhibited by some experimental data. In an attempt to account for this tailing, a "three-regions" model may be proposed (Srivastava and Rao, 1970). Extensive tailing is hypothesized to result from an additional interaggregate diffusion mechanism. The aggregate is conceptualized as consisting of two distinct porous regions: micropores and macropores. The additional resistance, then, is a result of diffusion transfer between the micropores and macropores regions. This dual interaggregate-porosity model was constructed by combining concepts from the two-region models presented above with the bidisperse-particle model used in chemical engineering. The resultant is a porous medium consisting of three porous regions: micropores (intraaggregate porosity), micropores (interaggregate microporosity), and macropores (interaggregate macroporosity).

For the dual interaggregate porosity model discussed above, the immobile region was divided into two sub-regions in order to obtain a total of three distinct regions. A three-region model may also be developed by dividing the immobile region into one sub-region. Such a model was proposed by Srivastava et al. (1970). Adsorption-desorption micropores is assumed to occur in both the "rapidly sorber" and

'moderately mobile' regions, while more transfer is assumed to occur between the rapidly and moderately mobile and the moderately mobile and immobile regions.

The bimodal characterization of the mobile (Harrison et al., 1988) or immobile (Korwar and Rao, 1988) domains employed by the above models is in direct contrast to the unimodal characterization employed by the Mankiwian models. It is very likely that a distribution of past shocks, rather than one distinct class, exists within an aggregated unit. Thus, a three-region characterization may more accurately represent some conditions. It may be sufficient, however, to quantitatively distinguish the mobile or immobile property into two distinct functions. In any event, such a distinction is probably not necessary for a process where interaggregate mobility is not extremely large. The Mankiwian (i.e., two-region) models, therefore, are probably sufficiently accurate for most soils.

Ultimately, the two- and three-region models are simple approximations of true process soils. Higher-order models could be developed by progressively increasing the number of explicitly defined regions (i.e., 8 regions and 8-1 more transfer mechanisms). Ultimately, this characterization will lead to a continuous probability (or probability density) distribution function. For example, a stochastic function model (Jury, 1981; Jury et al., 1986) considers a continuous past-soil velocity distribution. Past-soil distribution, estimated using a rapidly mobile model, has been utilized in the past to model solute transport (Manderson and Bennett, 1976). Because more transfer between

the price was not included, the model performance was poor (Zhu et al., 1999).

Receptance-Induced Reorganization

The occurrence of RE during vehicle response to vibrational noise is well documented, as discussed above. There exists, however, a significant amount of published data about consistent behavior as exhibited in the absence of RE, for example, connecting vehicles exhibiting symmetrical 90° phase velocity relative to one (cf. Elrod et al., 1981; Swadlow and Chang, 1979; Lee et al., 1979; Wood-Rizzo et al., 1987; Bushard et al., 1987; Lee et al., 1988). Such behavior suggests that the reorganization is a result of a response-induced mechanism (Breneman and Lee, 1994). Response reorganization (RR) can result from either changed reorganization or instantaneous diffusion (Breneman and Lee, 1994). Classical reorganization results from inter-related interactions between the vehicle and specific response sites of the vehicle. Reorganization resulting from instantaneous diffusion involves the diffusion mass transfer of vehicles within the vehicle matrix. Although both RE and instantaneous diffusion involve a diffusive mass-transfer mechanism, they are considered different because RE is predominantly a pair-diffusion process, while instantaneous diffusion is more similar to a multi-diffusion process. The results of several recent experimental and theoretical analyses (Bushard et al., 1987; Breneman and Lee, 1994; Wood-Rizzo et al., 1997) suggest that response reorganization for vehicle channels may, in many cases, be controlled by non-related interactions between the vehicle and roadway.

organic matter. It is important to note that, in contrast to 195, 196 influences only working solutions.

The first to recognize the effects of non-equilibrium on solute desorption was Wilson (1944)—she stated “the width of a band (chromatographic plate) may increase because the leading edge of the band migrates too rapidly on account of a low rate of adsorption, or because the trailing edge of the band migrates too slowly on account of a low rate of desorption”. Early attempts to model solutes as small spherical particles involved simple “one-way” first-order models in which the sorption rate is taken as a function of the concentration difference between the solid and solution phases (cf., Collins et al. 1979). This approach was based on that taken by researchers in chemical engineering (e.g., Levens and Amundson, 1962). This model has failed to predict experimental data (e.g., Schwabach and Marshall, 1961, Rao and Francis, 1961; Yu and Schowen, 1966; Branton and van der Pui, 1969). Sorption data from batch experiments have been found to exhibit a two-stage approach to equilibrium: a short initial phase of fast uptake, followed by an extended period of much slower uptake. This pattern is followed by most, if not all, sorption reactions (Gaffs and Porras 1961, Yu and Schowen, 1966). Recently, roughly 50% of the sorption occurs within the first few minutes to hours, with the remainder occurring over periods of days or months (e.g., Horikawa, 1969; Bielef and Agle 1969; Oliver, 1970; Bell and Roberts, 1969, Ganes and Klemm, 1964). This type of behavior lends itself readily to approximation with a two-stage approach. Models formulated with this

conceptualizations have been variously called "instantaneous", "open", "unresponsive", or "inactive" models.

In these models, conceptualization is assumed to be the result of a time-dependent receptor reaction of the vehicle with the surface. Receptor may be represented by two channels, reacting either in series or in parallel, with the latter being the more common biochemistry conceptualization. The receptor is hypothesized as having two receptor domains, where receptor is instantaneous for one and is rate-limited for the other. Receptor for the biochemically-controlled domain is described by a first-order rate equation, while the other domain is represented by an equilibrium isotherm equation. It should be noted that as long as one of the domains is equilibrium controlled, the series and parallel conceptualizations are mathematically indistinguishable (Karlstedt, 1966; Karlstedt and Morris, 1965). Also, the equilibrium-controlled domain can be replaced such that both domains are kinetic controlled. The suggestion that the existence of a second, kinetically-controlled class of receptor sites may be responsible for observed HIF asymmetry was first made by Hobbings and Spring (1961).

Receptor models, with one domain equilibrium controlled, were developed by Holm et al. (1956) and Cannon and Klotz (1971), while Holm et al. (1956) and Karlstedt (1965) presented models where both domains were rate limited. The one-site model mentioned previously is a special case of the two-site model, where all receptor sites are assumed to be of the time-dependent class (Holm et al., 1956; van Gerschten, 1961). The two-site model has generally been able to represent conceptualization data better than the one-site model.

The two-site receptor model may be represented in the following manner:

$$R = R_1 + R_2$$

where R = solution-phase concentration (R_0/V_0), R_1 = monophase concentration (R_1/V_1) for equilibrium sites, and R_2 = monophase concentration (R_2/V_2) for kinetic sites. Assuming that the Langmuir equation is applicable to both groups of sites, the total receptor concentration at equilibrium (R_0) is given by

$$R_0 = R_1 + R_2 = R_0 / D^2$$

where

$$R_1 = F R_0 / D^2$$

$$R_2 = (1-F) R_0 / D^2$$

The distribution between the two types of sites is described by F , defined as

$$F = R_{01} / R_0$$

where R_{01} is the receptor partition coefficient for the equilibrium sites ($R_1/V_1 / R^0$) and R_0 is the receptor partition coefficient for the whole cells ($R_0/V_0 / R^0$).

The two-site model may be written in the following mathematical form:

$$\begin{aligned} \frac{dR}{dt} &= (R_0 - 1) \alpha R^2 - \frac{dR}{dt} = (1 - F) R_0 \frac{dR}{dt} = \\ \frac{1}{F} \frac{dR_1}{dt} &= \frac{dR}{dt} \end{aligned} \quad (3-6)$$

$$(1 - F) R_0 \frac{dR}{dt} = - \alpha (R^2 - R^0) \quad (3-7)$$

by defining the following dimensionless parameters:

$$\sigma^2 = R_0 / (1-\beta) R_0 \sigma_0^2$$

$$R_0 = 1 + (\lambda/\beta) R_0 \sigma_0^2$$

$$\sigma = R_0 (1-\beta) R_0 \sigma_0$$

$$\beta = [1 + (\lambda/\beta) R_0 \sigma_0^2] / R_0$$

where R_0 is the main transfer rate coefficient ($1/\tau$), and σ is the Frenkelian nonlinear absorption coefficient coefficient. Now that, in contrast to many earlier models which have employed linear Lindholm (a $g_{\perp}$ two function, 1961; Betti-Glass et al., 1984) the Frenkelian Lindholm is used to represent absorption coefficient. Thus, Landau nonlinearity can also be accounted for with the equations presented above. In the model formulation of Bellin et al. (1974), which was in dimensional form, nonlinearity was included as well.

The distribution of the excited surface ions (or, parallel) classes of atoms differing in reaction time may be extended to accommodate any number of classes, each with its own unique rate constant. For example, Houston et al. (1980) present a theoretical model. The starting case would be a continuous distribution of rates and associated rate constants. A model describing this case has been developed by Williamson (1974), where the atom population is represented by the transfer time distribution (i.e., rate constant distribution).

Simplification

The models employing the diffusion equation are theoretically pleasing because they employ a truly mechanistic approach. These models have been successfully used for simplified systems. However, once real soil is considered, with all its complexity, the usefulness of these

models become questionable. For example, to apply these models the size and shape distribution of the macromolecules (e.g., aggregates) are required. Determination of these distributions, especially at the final state, is not viable under most conditions.

It must be stressed that these models have been developed to represent systems influenced by DR. Application of these models to systems influenced by processes other than DR can result in erroneous results. For example, Miller and Weber (1981) applied an inter-aggregate diffusion-based model to the transport of organic solutes (chlorine, nitrobenzene) through packed cell columns. The inter-aggregate diffusion coefficients, determined by optimization of data obtained from batch experiments, were on the order of 10^{10} cm²/year. These values are several orders-of-magnitude smaller than those reported for typical soils (e.g., 10^{11} - 10^{12}). Such a discrepancy suggests that the observed non-equilibrium is the result of some process other than simple diffusion into cell aggregates. A similar application of a diffusion-based model was made by Rotter et al. (1982), who studied the transport of chloride, nitrobenzene, and benzene through columns of packed soil. They utilized aggregate radius as the fitting parameter, the values determined were appreciably less than larger than those measured. This again suggests that a process other than inter-aggregate diffusion was responsible for the observed non-equilibrium.

The physical mass-transfer (i.e., two-region) and the invasion-erigthen models have been shown to be mathematically equivalent for the binary interface case when retention is distribution-free (van Duynhoven, 1981; Rodi-Kane et al., 1984). Hence, they produce similar fits to

experimental data (Mac OS al., 1977; Barth-Clark et al., 1984). The two-site receptor model may also be used to represent ion-channel diffusion (Strassman and Lee, 1987). Hence, the mathematical representations for all these nonequilibrium processes are equivalent. This means that similar should be employed in designing the mechanism(s) responsible for nonequilibrium activity on the basis of curve fitting models to experimental data.

A major advantage of the none-transfer models over the diffusion-based models is that a description of the structure of the protein motion is not required. This, perhaps, explains their much wider use. There are conditions, however, under which the none-transfer models can not represent observed behavior: a) $\bar{g}$: the distribution fits data not sometimes observed: a non Gaussian distribution, rather than the uniform facility in particular distributions as reaction rates assumed by the Hixonian models; say in a non stochastic representation of time conditions. However, the number of parameters involved with such a model greatly exceeds our present capability to independently evaluate the processes represented by these parameters. Both models could, therefore, be considered as operating in a collaborative mode.

Several types of mechanical models exist for characterizing enzyme-transporter under nonequilibrium conditions. Each has advantages and disadvantages. The choice of model is constrained by available data and the purpose of the modeling effort. It is essential to distinguish between mechanical models and the conceptual models they represent. The use of any mechanical model should be based on a sound understanding of the processes being modeled.

CHAPTER 2 PRELIMINARY CONCEPTS

The purpose of this work was to investigate, at a mechanistic level, the processes responsible for the phenomenon of nonequilibrium sorption. An additional objective was to develop conceptual and mathematical models for the transport of solutes influenced by nonequilibrium sorption. A brief introduction to the transport of solute in absorption systems and current modeling approaches is presented in Chapter 1. Experimental techniques, namely dilute displacement, flow-interruption, and gas-pulse desorption, are developed and evaluated in Chapter 2. The processes responsible for sorption nonequilibrium are investigated in Chapter 3, where the methods developed in Chapter 2 are employed to study the influence of chemical properties of the solute and the solution on sorption kinetics. A conceptual and mathematical model for simulating the transport of solutes influenced by multiprocess nonequilibrium is developed and evaluated in Chapter 4. Solute transport at the field scale is investigated in Chapter 5, a model that accounts for multi-scale and scale-dependent nonlinearity is developed.

CHAPTER I
EXPERIMENTAL APPROACHES FOR INVESTIGATING CORRUPTION BEHAVIOR

Evaluation of Methods for Investigating Corrupt Behavior

Introduction

The corruption behavior of organic chemicals has recently become an active area of research. In the investigation and modeling of corrosion dynamics it has generally been assumed in the past that the corrosion kinetics was sufficiently fast such that the local equilibrium assumption (LEA) was valid. Studies of corrosion kinetics have, until the past few years, been performed almost exclusively with the batch-cell method. The results of these studies appeared to substantiate the validity of the LEA. Recent experimental and theoretical investigations have, however, caused the validity of the LEA to be questioned. The adequacy of the batch-cell method for investigating the corrosion kinetics of organic chemicals is also questionable, given the discrepancy between kinetics obtained with this technique and with many methods.

Several methods have been developed that may be used as an alternative to the batch-cell method. The two that have received the greatest use are the gas pump (GP) and the molecular displacement column (MDC) techniques. The GP technique was first applied to corrosion by Kuntzeff (1988); she investigated the autocatalytic corrosion of polymeric materials from dicarboxylic esters. The GP technique has

which have been used by others (Charltonoff and Harris, 1981; Oliver, 1989; Deane and Elmore, 1989). To employ the SF technique, a reactor containing a pre-equilibrated slurry of solvent, solute, and water is purged with a gas such as air or nitrogen. The gas stream strips the solute from the water phase, thus inhibiting desorption of the solute from the solvent. The gas stream is trapped in a closed open ending the reactor to allow determination of mass flow of solvent. A mathematical model is "fit" to the experimental results to determine values for kinetic parameters. This technique as described above provides data only for the desorption phase. A modified approach was utilized by Yu and Anderson (1988) to investigate both absorption and desorption phases. The apparatus was designed to operate under closed conditions to prevent mass loss. To operate in such a manner, a nondestructive detector is required. A photoluminescence detector (PLD) was employed by Yu and Anderson (1988).

Black's displacement technique has been widely used in chemical engineering, petroleum engineering, and soil science to investigate various aspects of dispersion, sorption, and transport of solutes. One of the first techniques to investigate the nonequilibrium sorption or sorption kinetics of organic solutes was initiated by full academics (e.g., Fittick et al., 1966; Ray and Black, 1967; Bevilacqua et al., 1968; Bevilacqua and Chang, 1974; Green et al., 1976; Brown et al., 1975), who were evaluating the behavior of pesticides. The SF technique has since been used to investigate the sorption kinetics of other types of organic chemicals, such as chlorinated compounds and alcohols (e.g., Schramm and Warner, 1981; Lee et al., 1983).

There has been to date no critical evaluation either of the general applicability or the expediency of these two techniques. This paper reports the results of experiments that were conducted to establish the conditions under which the two techniques are viable. Various modifications that enhance viability are discussed. The performance of the two techniques is compared.

Background and Rationale

Background and Method

Experimental questions. A disadvantage of the Kerkhoff apparatus is that it can only be operated in the description mode. A disadvantage with the design used by Yu and Lebedev is that description can only be studied with the dilution approach ($C_1 \ll C_2$). A given volume of anti-solvent elutri is a condition of equilibrium is diluted by adding a given volume of "solvent" water (which features description). Another disadvantage is the diffusion limit associated with the PCB. This would be of special concern for solutes with very low solubilities, small changes of which concentration levels may not be discernable. In such cases the design used by Kerkhoff (1960), where a trapping device is employed, would be advantageous. The apparatus employed herein was designed to combine the advantageous features of the Kerkhoff (1960) and Yu and Lebedev (1964) designs and to eliminate the associated disadvantages.

The general design was based on that of Yu and Lebedev (1964). A one liter glass reaction vessel, was connected to a stainless steel bellows pump (BB-11, Royal Crown Co., Dayton, OH). The flow generated

with the pump was converted to a closed loop all-glass system; a small portion (approximately 20 cc/min) of the flow was diverted through a parallel loop in which a flow through photoionization detector (Purdie; linear F1 50-51) was attached. The potential for mass loss from the system (i.e., leakage) was evaluated by injecting a known mass of solute into the closed system and measuring the output signal for decay; a steady response was observed over a time frame greater than the length of every experiment. A second closed loop bypassing the transfer was utilized to determine base line detector response. The FID was located in a gas chromatograph (Purdie linear flow lines 1000); the detector was maintained at a temperature of 150°C to prevent vapor condensation. The detector output signal, representing the gas phase concentration of the solute, was recorded by a Linear Model 1000 chart recorder.

Modifications to the system included the following:

1) Three way valves were placed in-line so that the apparatus could be operated in either open or closed modes. This allowed the performance of an adsorption experiment in the manner of Yu and Bartholomew (1980) and then, with the same slurry, the performance of a desorption experiment in the manner of Bartholomew (1980); 2) an in-line detuning valve was employed to control the gas flow. This enhanced the ability to equilibrate experimental conditions. 3) An additional valve was employed to allow use of trapping devices when concentrations were such that detection by FID was not viable.

The purge gas was treated by active distillation to remove contaminants and was passed through a water purge vessel to remove water

operation prior to entry into the system when the apparatus was operated in the open mode.

Reagents The following chemicals were used: hydrogen, chloroform, 1,1-dichloroethane, 1,1,1-trichloroethane, isonitrosomethane, and vinylacetylene. Pure solids and liquid materials were used in the experiments. All solids and liquid materials were passed through a 1 μ m sieve. The best that can be done practice was utilized for all experiments.

Experimental procedure Only the results of the open-mode (i.e., desorption) experiments are reported herein. For these experiments measured quantities of adsorbent, adsorbate, and solute were placed in the reaction vessel, which was then sealed and placed in a refrigeration shaker for 48 hours to allow the establishment of equilibrium. After the equilibration period, the vessel was returned to the experimental apparatus and the system was operated in the closed mode to determine the equilibrium gas-phase concentration of the solute. With this value, an equilibrium sorption constant (K_s) could be determined given the following quantities: gas volume (V_g), water volume (V_w), adsorbent mass (M_s), solute mass, and Henry's constant (H).

Values for all of the quantities mentioned were determined by measurement except for H , values of which were taken from Johnson et al. (1984). Once a steady output signal was established, the system was operated in the open mode to allow gas purge desorption.

Prior to the desorption experiments, calibration curves were obtained for each of the detectors by monitoring the response of the detector to known inputs of solute into the system. The signal output

of the detector recorded during a desorption experiment were converted to concentrations with the concentration detector response function determined with the calibration curve. The detected responses for all experiments were within the range covered by the calibration curve.

Modeling. Early attempts to model sorption kinetics employed a "one-site" model where all sorption is sites identical. This approach has failed to adequately represent experimental data (e.g., Schwarzenbach and Westall, 1981; Lee and Jirassak 1983; Wu and Gschwend, 1986; Jirassak and van der Pui, 1988). Sorption data have been found to exhibit a two-stage approach to equilibrium: a short initial phase of fast uptake or release where roughly 50% of total sorption occurs within minutes to hours, followed by an extended period of much slower uptake occurring over periods of days or weeks (e.g., Karickhoff, 1980; Ball and Roberts, 1981; Karickhoff and Morris, 1985; Ball and Aja, 1985; Olsson, 1986; Jirassak and Eisenreich, 1988; Wu and Gschwend, 1984). This type of behavior is usually approached with a bi-sorption approach. Thus, the results of the 12 experiments were fit with a bi-sorption model to determine values for the two kinetic parameters k_1 and k_2 .

The system is conceptualized as follows:

$$C_g \xrightleftharpoons[k_2]{k_1} C_w \xrightleftharpoons[k_3]{k_4} C_s \quad (1-1)$$

where C_g is the solute concentration in the gas phase (M/L^3), C_w is the solute concentration in the water-phase (M/L^3), C_s is the sorbed-phase concentration in the equilibrium domain (M/M), k_1 is the sorbed-phase concentration in the kinetic controlled domain (M/M), and k_2 and k_3 are

the forward and reverse sorption kinetic constants (T°), respectively.

The two adsorbed-phase concentrations are defined as

$$A_1 = F A_2 C_0 \quad (1-1a)$$

$$dA_2/dt = k_1 A_1 + k_2 A_2 - A_2 = (1-F) A_2 (dA_2/dt) = \text{net } \pi \text{ system} \quad (1-1b)$$

The total mass of solute in the system (M_0) is given by

$$M_0 = (F A_2 C_0) + (A_2 dA_2/dt) + (A_2 F A_2 C_0/dt) + (A_2 A_2) \quad (1-1)$$

The mass flow of solute from the reactor is given by

$$dM_0/dt = -q A_2 = A_2 (dA_2/dt) + A_2 (dA_2/dt) \quad (1-1)$$

where $A_2 = A_2 + (A_2/dt) + (A_2 F A_2/dt)$. Equation 1-1 may be rewritten in conventional form and is a second order linear ordinary differential equation, which can be solved analytically.

The model required the data to be in terms of cumulative mass flow of solute out of the system. This quantity was obtained by repeated integration of the concentration-time data. Knowledge of the following parameters are required to run the model: A_2 , A_2 , gas flow (q), A_2 , A_2 , A_2 , mass of solute, A_2 , T , and A_2 (function of total solute mass removed from reactor). The value for A_2 was determined as discussed above, values for A_2 were taken from Schwartz et al. (1980), all other parameter values, except for A_2 , F , and A_2 , were measured. Values for A_2 were obtained by dividing the total quantity of mass measured from the reactor by the input mass. Flows in all cases the experiments were run until the baseline value (i.e., "zero" concentration) was reached, A_2 represents the function of mass lost during the experiment, including the equilibration step. Considering the nature of the chemical and the relatively short time involved, this loss is most likely a result of volatilization from the reactor during the equilibration period and

during the time when the monitor was attached to the apparatus. This loss was less than 1% in all cases and closer to 1% in the next experiments. This loss does not affect accurate determination of kinetic parameters as it is accounted for in the model. With the approach described above all parameters except k_2 and F were independently determined. These two kinetic parameters were determined by optimizing the fit of the model simulation to the experimental data Kinetic displacement method

Experimental apparatus The techniques employed for the kinetic displacement experiments were similar to those utilized by Ward-Cross et al. (1987) and Lee et al. (1988). The column apparatus was an HPLC/HPLC preparative chromatography column (Beckman) made of polished, heavy borosilicate glass, with an internal diameter of 1.2 cm. An adjustable stack was employed such that the length of the packed column could be varied up to 25 cm. Red supports on both ends were used for better diffusion made in contact with a porous Teflon filter disk of pore size 10 to 15 μ m. The diffusion such enhanced control classification of infused solution and size isolated dispersion at the effluent end. The column apparatus was designed to have a minimum void volume in the end plates. Two single-plasma HPLC pumps (Shimadzu Medical Electronics, Model 10A) were connected to the column with a Rheodyne switching valve (Model 1040) to facilitate switching between solutions with and without the release of ligand. The system was designed so that the mobile contained only solutions with or without.

Effluent from the column was directed through a flow-through, variable wave-length UV detector (Shimadzu) to allow simultaneous

monitoring of the solution phase concentration of the solute, which was recorded on a strip chart recorder (Linnar Model 1200). Previous electric displacement studies have usually employed collection of effluent fractions, which were then analyzed by GC or HPLC. For volatile chemicals, this method suffers from the potential for loss by volatilization during the fraction collection and analysis steps. The use of the flow through detection method eliminates this problem. It also significantly simplifies the analytical process. However, this method is limited to a specific set of chemicals.

To compare the performance of the flow through and effluent fraction detection methods, a electric displacement experiment was performed wherein an automated fraction collector (Linnar Model 1200) was interfaced in series to the UV detector. Samples collected with the fraction collector were analyzed by HPLC (Gutro Instrument, Model 400 UV detector) (Gutro Instrument, HPLC 100 automated sampler). In this manner, a HPLC could be measured essentially simultaneously with the gas chromatographic analysis. A volatile chemical, acetone, was selected so that any observed difference in RRTs obtained with the two methods could be a result of factors other than volatilization. The results of this experiment are shown in Figure 3-4. There is obviously no difference between the two RRTs, from which it may be concluded that the two detection methods yield comparable results.

Chemicals The following chemicals were employed for the electric displacement experiments: tritiated water, hexane, chloroform, 1,2-dichloroethane, 1,3,4-trichlorobenzene, trichloroethylene, trichloroethane, and acetone. Radio mill was used for shape

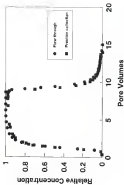


Figure 1-1. Comparison of distribution methods, data are for aqueous and benzene sol.

experiments. As for the gas purge experiments, the oil seal fraction was used for the column experiments.

Experimental procedure. The column was packed in incremental steps with the dry material to establish uniform bed distribution. After completion of packing, electrolyte solution (0.1 M CaCl_2) was pumped through the column until steady state water saturation was established, which generally required approximately ten days. The consistency of column output ($\lambda = 1$, achievement of saturated conditions) was monitored periodically throughout the experiments. When the column was tested, it was carefully disconnected and mass balances in pure water and deaerated water ($\lambda = 1$, flux associated with the column expansion) were obtained. The measured dead volume was used to determine the corrected pore volume of the column.

The supporting electrolyte for all solutions was CaCl_2 (0.1 M). Saturated stock solutions were prepared for each solute by placing quantities in excess of solubility in contact with the electrolyte solution and allowing the solution for at least 48 hours. Solutions were filter sterilized with 0.45 μ m filters prior to use. Aliquots from the stock solution were diluted with electrolyte solution until the desired concentration was achieved. The λ_0 values for the experimental solutions were generally 20% of the aqueous solubility.

A typical experiment involved the continuous injection of a pulse of the selected solute, the pulse also being large enough such that the point of $\lambda/\lambda_0 = 1$ was reached. The solute pulse was then displaced with 0.1 M CaCl_2 solution until the point of $\lambda/\lambda_0 = 0$. Consistency of flux was periodically checked by collecting effluent fractions. These

measured flow rates were checked against the average flow rate determined by collecting and measuring all effluent over the injection period. They agreed well in all cases. The flow rates used for all experiments were approximately 1 ml/min ($v = 50 \text{ cm/hr}$). The properties of the Hecla column were as follows: $L = 1.5 \text{ m}$, $\rho = 1.70 \text{ g/cm}^3$, $\epsilon = 0.445$.

Data analysis. The results of the isochloric displacement experiments were analyzed with a Blackstone model to avoid equivalency with the data analysis procedure employed for the gas-phase experiments. Models of this type, where sorption is assumed to be instantaneous for some portion of the process and non-Fickian for the remainder, have been presented by Deiss et al. (1984), van den Hulst and Knaflitz (1990), and Hansen and Klein (1997). These models can represent each of the three processes: nearly physical nonequilibrium, chemical nonequilibrium, and bi-directional diffusion, responsible for nonequilibrium sorption (Hansen and Kim, 1998).

In isochloric solute transport, the following two-dimensional equations are employed:

$$\partial C^2 / \partial y = (2\alpha - 1) \partial C^1 / \partial y + (1 - \beta) \partial C^0 / \partial y = (1/\Gamma) \partial^2 C^2 / \partial t^2 - \partial C^2 / \partial t \quad (3-5)$$

$$(1 - \beta) \partial C^1 / \partial y = \alpha (C^2 - C^1) \quad (3-6)$$

where

$$C^2 = c_2/c_0 \quad (3-7a) \quad \alpha = \alpha_2/\alpha_1 \quad (3-7b)$$

$$\beta^* = b_2/(1 - b_1) \quad (3-7c) \quad \beta = 1 + (c_0/\Gamma) \alpha_1 \quad (3-7d)$$

$$\gamma = \alpha_1/\Gamma \quad (3-7e) \quad \beta = (1 + b_2/\Gamma \alpha_1) \gamma \quad (3-7f)$$

$$\Gamma = \alpha_1/\epsilon \quad (3-7g) \quad \alpha = b_2(1 - \beta) \alpha_1/\alpha \quad (3-7h)$$

and where ν is the dispersed coefficient (m^2/T), $\bar{v}$ is the average pore-
volume velocity (m/T), x is distance (L), h is column length (L), ρ is
bulk density (kg/m^3) and f is volumetric adsorption constant. Note that
the kinetic parameters k_p (first order rate constant) and F (fraction of
adsorbate with instantaneous sorption) are equivalent to the two kinetic
parameters contained in the model used for the analysis of the gas-phase
data.

To run the model, knowledge of the following parameters is
required: the Péclet number Pe , which represents the dispersion-flow
contribution to transport; the retardation factor R , which represents
the effect of sorption on transport; the fraction of instantaneous
sorption, F ; the Bodenstein number α , which is a ratio of hydrodynamic
radius to characteristic size of the sorption "residual"; and
 T_p , the time to pore volume of the input pulse. The value for F was
obtained from the HPL of a connecting column, indicated earlier. The
value for R was obtained by mass analysis, i.e., the direct
normalized, absolute temporal moment of a dilute pulse. The general
equation for the first moment is defined as

$$M_1 = \int_0^\infty t C_p dt / \int_0^\infty C_p dt \quad (3-6)$$

Application of eq 3-6 to a HPL will not directly yield a value for R for
a non-flow input pulse, i.e., when T_p is infinite. A correction factor
of 0.571 (Galembi, 1981) was applied to quantities determined with eq
3-6 to calculate the R value. The value of k_p was known from
experiments. The two unknown parameters are then β and α . The
nonlinear least-squares optimization program GTESS (van den Hul,
1981) was used to determine values for the two unknown

Results and Discussion

Gas-phase experiments

The results of gas-phase desorption experiments performed with the weak HCl and Br₂ solutions (benzene (BZ), chlorobenzene (CB), 1,2-dichlorobenzene (DCB), and 1,3,4-trichlorobenzene (TCB)) are presented in Figures 3-3. Note that the time required for desorption was a function of the solute, with BZ requiring the least amount of time and TCB the most. The relationship between k_p values of which were determined by optimization, and k_d was evaluated using the Thomas-Frost energy-relationship technique, in the manner of that to be discussed in Chapter 4 of this dissertation. The results are shown in Figures 3-5 in which correlation between k_p and k_d is evident. Such a relationship has been observed by others (Kricheldorf [198], Kricheldorf and Merz, 1980) and, for the types of systems investigated herein, is suggestive of an intermolecular-diffusion process (Kricheldorf and Merz, [198]).

Previous gas-phase experiments have been performed for chlorobenzene by Kricheldorf and Merz [198], Silver [198], and Ba and Redmond [198]. To compare the results obtained by these researchers to those obtained herein, values for k_p and k_d obtained from the research reports are plotted in Figures 3-5. A combined regression of the literature and experimental data yields an r^2 of 0.89. With such a good value it is apparent that the experimental results obtained herein are comparable to those obtained by the other researchers. The SF technique would, therefore, seem to have associated with it a high degree of reproducibility and consistency.

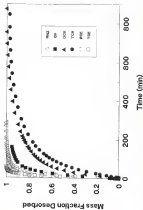


Figure 2-3 Results of gas purge experiments 400-700 for SO₂, CO₂ and TCO₂ from basalt melt.

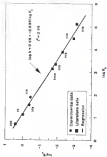


Figure 1-2 Relationship between R_p and R_s

The results of the experiments for desorption of isopropylmethane (ICE) and isobutylmethane (IBE) from Bentin soil are presented in Figures 3-1. Note that, as was the case for the other families presented in Figure 3-2, the desorption rate was a function of the solute with ICE requiring more time than IBE. The values for k_d and F determined by optimization were 16 hr^{-1} and 1.30 for ICE and 1 hr^{-1} and 0.18 for IBE. These values will be used later in attempting to predict RTD obtained from simulated displacement of ICE and IBE through a Bentin-soil column.

Gas-gauge experiments were performed with TCE and six other solutes and equidur materials in addition to Bentin soil. The k_d values determined from these experiments are compared in Figure 3-4 to the regression equation reported in chapter four of this dissertation for data obtained with the gas-gauge method. The data compare relatively well to the regression line, especially considering that some of the chemicals comprising the data set used to develop the regression line were chlorobenzenes. These results further support the reproducibility and consistency of the DF technique.

The two equations shown in Figure 3-4 represent the independent values of the families obtained for the two equidur materials. The characteristic reaction time of TCE compares to these two materials was fast enough such that the desorption curve could not be distinguished from the curve established by stripping TCE from solution containing no solvent (i.e., gas-stripping curve). To have confidence in the kinetic parameters determined from a DF experiment, there must be a significant difference between the desorption and gas-stripping curves. In other words, the characteristic time of the desorption reaction ($1/k_d$) must be

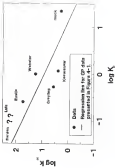


Figure 3-4. Trends of the gas-phase equilibrium, T experimental independent values of K_b

greater than the characteristic time for gas-liquid mass transfer (t_{Lg}). Given the known relationship that applies to water between k_L and k_g , the condition under which k_L is t_{Lg} and thus under which the CF technique would be viable, is strongly controlled by the sensitivity of the specific volume/mass ratio. Based on the studies presented in Figures 3-3 and 3-4, it appears that the CF technique is viable for systems having k_g values ranging from over 100-000 to less than 10, and becomes unreliable for k_g values in the vicinity of 0.1 m/s.

Relative Diffusivity Measurements

A relative water RH was obtained for the values to establish the hydrodynamic character and to determine a value for β (see Figure 3-2). This RH was symmetrical and elongated in shape and was identical with gas-water solubility which suggests the absence of physical nonequilibrium (Gossens and Rao, 1989). RHs for H₂O, CH₄, 1,1-dichloroethane (DCE), and THF are presented in Figure 3-5. Note the symmetry of the RHs) data. In conjunction with the symmetrical RHs obtained for crystalline water, is highly suggestive of a surface-related nonequilibrium process (Gossens and Rao, 1989).

Values for k_L and k_g obtained from these experiments are plotted in Figure 3-6, along with the values presented in Figure 3-3 that were obtained from the gas-purge experiments. The similarity between the two data sets suggests that the two experimental techniques produced comparable results. It is also evident that no known relationship between k_L and k_g is displayed by the RSC data.

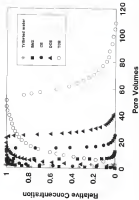


Figure 3-5 Relative of solute displacement experiments for different solutes

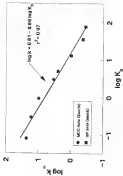


Figure 3-4 Comparison of results obtained from the BIC and BIC methods

The comparability of the two methods was further tested by attempting to use kinetic-parameter values determined by gas-purge to predict a TTC obtained for the same cell/polymer pair. The IFN obtained from steady-state displacements of PCL through the barrier cell column k_p presented in Figure 3-7. The values for k_p and β determined from the butylis/PCL gas-purge experiments were used to calculate values for β and α (see eq. 3-7f and 3-7g). The simulation predicted by the bi-directional model with these independently-determined kinetic parameters is shown in Figure 3-7. The model simulation compares extremely well with the experimental IFN. A similar attempt was made to predict the TTC obtained from steady-state displacements of PCL through the barrier column. (See Figure 3-8). The prediction, while fair, is not as good as that obtained for PCL. This may be a result of the lower k_p value for TIL (8 IFN) which is within the range where the IF envelope may be unstable. These two predictions to my knowledge represent, along with that reported in Chapter 2 of this dissertation, the first successful cases where non-equilibrium IFNs of organic solutes were predicted with all parameter values being obtained independently (i.e., without curve fitting).

It appears that the gas-purge and steady-state displacement techniques yield comparable results, based on the data presented in Figures 3-4, 3-7 and 3-8. This would suggest that the two methods are measuring the same physico-chemical process. This also suggests that the bi-directional model, since it was used successfully in data analysis for both methods, provides a valid representation of the process responsible for the observed non-equilibrium behavior in any case. The parameter k_p , rather

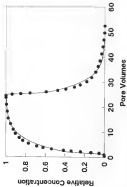


Figure 2-3. Evolution of POC SEC

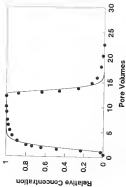


Figure 3-4. Evolution of TOC (ppm)

Thus being just a firing function, say that he considered as being representative of the nonequilibrium mechanism.

The algebraic displacement technique as described is especially useful for self-compensating systems. Its efficacy, however, is greatly reduced for systems composed of highly sensitive channels or of cells containing high levels of either one/ or several active ions the sensitivity of the system increases both the uncertainties and problems such as overlap in the spectrum become of increasing concern. These problems can be alleviated through modification of the experimental method. One such approach involves the use of chemical organic solvents. The presence of solvent yields in reduced values of k_p (Das et al., 1965; Sheth-Datta et al., 1971; Fu and Lohp, 1974; Sheth-Datta et al., 1971) and in increased values of k_p (Sheth-Datta et al., 1971). With these effects, the use of solvent can significantly reduce the experimental time and the occurrence of other problems associated with the use of highly sensitive channels. It will be shown in Chapter 4 of this dissertation that values for k_p in aqueous systems can be calculated reasonably by extrapolation from experiments performed with alcohol-solvent systems.

The determination of kinetic parameter values from solvent experiments is predicated upon the ability of the mathematical model to successfully simulate the experimental data. Confidence in the calculation of the parameter values as determined is obtained only with a unique solution (i.e., when one suite of parameter values provides a solution that is significantly better than all others). For many channels a system is near equilibrium or under extreme nonequilibrium,

attainment of a unique solution may prove difficult. A modified double-displacement technique, involving flow interruptions, that enhances the potential for achieving unique solutions, and that increases the robustness of optimal values of kinetic parameters, will be presented in the next section of this chapter. This method would appear to be especially useful for systems composed of equifor materials, as a low degree of noncollinearity may often be required for such systems based on their relatively low reactivity.

Conclusions

Two experimental methods for investigating noncollinearity aspects of organic chemicals have been evaluated. In planning to use either method it is important to consider their range of applicability. The viability of the gas-phase technique is controlled by the vapor pressure of the chemical and the reactivity of the solvent/surface combination. The method will obviously be applicable only for chemicals whose vapor pressure is such that gas-phase concentrations are of sufficient magnitude to be detected. The viable range of vapor pressure can be extended through the use of trapping devices. The viability of the double-displacement technique is questionable since k_p values are less than 0.1 s/l/g. Below this k_p value, the characteristic time of sorption is indistinguishable from that of gas-liquid mass transfer. The viability of the double-displacement technique is controlled by the reactivity of the solvent/surface combination and by the nature of the system. This technique is especially useful for systems composed of chemicals of low to moderate reactivity and of easily soluble or equifor materials.

The viable range may be extended with modifications such as solvent selection or flow interruption. Considering the results discussed above, the gas-purge technique would appear to be the method of choice for systems comprised of highly-reactive chemicals and especially for those with solids containing high clay or organic solvent contents. The adsorbate displacement technique would be the method of choice for systems of low and moderate reactivity.

The time required for desorption was observed to be a function of the volume, as the reactivity increased, the required time also increased. An inverse relationship between k_d and V_p was observed for the results obtained from both experimental techniques. This, in conjunction with the observation of asymmetrical RTCs for the sorbing solution and asymmetrical RTCs for the desorbing solute, suggests that the observed nonequilibrium was a result of an intramolecular-diffusion process.

Future Investigation: A Need for Investigating Sorption Kinetics

Introduction

Considering its importance, there is a definite need to investigate the occurrence of, and the processes responsible for, sorption nonequilibrium. Unfortunately, methods presently available are not capable of clearly delineating the operative mechanisms. Current practice often involves curve-fitting experimental data with various models and selecting the model that exhibits the best fit. However, the successful simulation of a data set by a mathematical model is a necessary, but not sufficient, condition for establishing the validity

of the underlying conceptual model. This is especially true when the mathematical equations associated with a conceptual model are non-linear, as they are in this case. The two-stage sorption model used to represent physical sorption/desorption has been shown to be equivalent to the two-stage sorption model used to represent chemical sorption/desorption for the case of linear sorption isotherms (van Osseltien, 1981; Knaflitz-Knaflitz et al., 1984). The two-stage sorption model may also be used to represent (an)isotropic matrix diffusion (KOH) (Gratwick and Rao, 1985; Lee et al., 1986). Generally, there is need for sophisticated techniques that can discriminate between the various sorption/desorption processes.

Under certain conditions, the processes of sorption/sorption/desorption cannot be readily discerned when analyzing data obtained with the typical column experiment. In these instances a technique that has a greater sensitivity to sorption/desorption would be very advantageous. When sorption/sorption/desorption is incorporated into solute transport models, parameter values are required for the kinetic terms. Under certain conditions, the current curve-fitting approach may not produce a unique set of values for a given set of parameters. To improve the efficiency of parameter determination, this ability must be enhanced.

The three issues discussed above are addressed in this section. A model for investigating sorption/sorption/desorption is presented. The model has a greater sensitivity to sorption/desorption and thus provides a greater capacity to investigate sorption/desorption. Because of this greater sensitivity, it also provides more reliable determinations of kinetic parameter values. In some cases, it may be possible to use the

methods to discriminate between the mechanism(s) responsible for sorption nonequilibrium. The conceptual and theoretical basis for the method is presented, and the application is illustrated.

Conceptual Basis for the Method

The method is based upon the so-called "interruption test" (Rudin and Myers, 1947; Newman and Blackwell, 1955) which has been employed in chemical engineering to elucidate whether species that are controlled by intra-particle diffusion or film diffusion. According to Hoffman (1962), this is the best technique for differentiating between these two rate-limiting processes. The technique involves placing the solvent into solution, removing the solvent for some period of time (the interruption period), and then reimmersing. If intra-particle diffusion is the rate-controlling process, solvents will continue to diffuse within the particle during the interruption period in response to intra-particle concentration gradients. In a sense, the solute uptake rate will be greater immediately upon reimmersion than it was just prior to interruption. If, however, film diffusion is rate controlling, the interruption will have no observable effect upon the solute uptake rate.

Rabin and Rudin (1961) employed the interruption method to substantiate intra-particle diffusion as the rate-determining step for the sorption of a series of nonelectrolytes on granular activated carbon. Recently et al. (1975) employed the method to investigate sorption kinetics of 1,4-dichlorobenzene on activated carbon and concluded that film diffusion was the rate-controlling process.

This technique may be modified and expanded to develop a method that not only can differentiate between film and interparticle diffusion, but also interparticle versus diffusion and rate-limited interparticle between surfaces and internal components of the surface. The major modification involves performing the test in a column, rather than in a batch system, hence the name—the flow interruption method. The method, then, involves displacing at a steady flow rate a solution containing the solute of interest into a water-saturated soil column, stopping the flow for some period of time, and then reinitiating flow either temporal changes in the effluent concentrations (1, 2), breakthrough curves (3,4) or concentration profiles within the column may be generated. The former is experimentally more feasible and is also theoretically more appealing since the temporal first moment (i.e., center of mass, equivalent to retardation factor) is independent of kinetic constraints, whereas the corresponding spatial moment is not (Bolin and Salama, 1981).

The flow-interruption technique is similar in operation to the so-called "stopped-flow" chromatography technique, first described by Kohn and Salama (1984). This technique, however, was developed to measure gas-diffusion coefficients and not to investigate sorption kinetics. The technique is employed by stopping the flow of carrier gas after the pulse has reached the midpoint of the column, and then reinitiating flow after some period of time. During the interruption, solute spreads only by molecular diffusion. In the absence of sorption or chemical reaction, the diffusion and dispersion processes are linear, and therefore additive. The influence of hydrodynamic dispersion and

uninterrupted boundary effluent can be estimated to determine the contribution of molecular diffusion to solute dispersion. The variance at several points of the BE (i.e., dispersion) varies with the length of interruption. Hence the slope of a plot of variance versus interruption time is proportional to the molecular diffusion coefficient. The method was recently verified by Selby and Saffari (1984) and Beck et al. (1987).

Mathematical Model

The kinematic model (eq. 1-6, 1-7) may be modified to simulate flow interruption by defining a modified pore volume parameter

$$p = \omega t^2 / L$$

where t^2 is elapsed time during periods of flow.

The above model may be used to represent any of the three following sorption nonequilibrium mechanisms—physical nonequilibrium, chemical nonequilibrium, or diffusional mass transfer of sorbate within solid and/or organic components of the sorbent.

The solute transport equations were solved under constant-flow boundary conditions and an initial condition of 0-0 using a Crank-Nicolson finite difference method. Numerical optimization was accomplished by coupling the modified model with a non-linear least-squares optimization program (NLS) (Dennis and Moré, 1984).

The Flow Interruption Process

When sorption nonequilibrium exists, flow interruption on the frontal side of a BE will result in a drop in the effluent solute concentration (except when flow diffusion controls the rate of sorption). An example of a BE obtained from a simulated flow-

Interruption experiment is shown in Figure 3-9. Points A and B in Figure 3-9 correspond to the pre- and post-interrupt effluent concentrations, respectively. The dip in the SEC is a result of sorption being a rate-limited, rather than instantaneous, process. Sorption will continue to proceed during the flow-interruption period thus reducing the in situ aqueous-phase concentration. The white concentration in the solution that is eluted when flow is recommenced is, therefore, lower than the concentration just prior to interruption. The non-linear portion of the SEC (labeled as I in Figure 3-9) represents elution of the interrupt-period residual solution. The subsequent portion exhibiting an increased slope (II) represents the breakthrough front of the solute pulse injected upon recommencing flow.

To maximize the magnitude of the maximum drop in effluent concentration, the interruption should occur within a specific range of Q' . This optimal range is dependent upon the sorptive and diffusive character of the chemical as well as the sorptive nature of the medium. Longitudinal diffusion of the solute in the resident solution can occur during the quiescent period as a result of concentration gradients along the column. Increased solute spreading resulting from molecular diffusion during cessation of no flow was demonstrated by Piggot and Wilson (1982b) and Pabst and Hatzispyros (1975). Molecular diffusion will re-distribute the solute from the region near the influent end (B-C) toward the region near the effluent end (D-E) thus increasing the post-interruption effluent concentration. Because such solute redistribution opposes the effects of rate-limited sorption, the true magnitude of the concentration drop can be masked. The lower the Q'

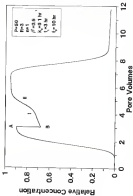


Figure 1.1: Simulated flow using the flow conservative method; t_0 = time of breakthrough, t_1 = time at which flow was stopped.

value the greater the intra-solvent concentration gradient and the greater the resultant solvent redistribution. Thus, to minimize the effects of longitudinal molecular diffusion, the flow interruption should be initiated at large enough C^2 values such that the in-solvent concentration gradient is small.

A flow interruption experiment which initiated water was performed to demonstrate the effect of longitudinal diffusion during the interruption period. Displacement of tritiated water through a column packed with Eucalyt Flow and Cs sandy soil with organic carbon content of 6.58% was stopped in the initial stage of solute breakthrough ($C^2=0.31$). The interruption period was approximately 22 hours. Upon resuming flow, the initial value of C^2 was 0.31. For a 50% mineral water solution experimental conditions but with no flow interruption, the relative solvent concentration in the effluent pore volume was approximately 0.28. Solute redistribution resulting from longitudinal diffusion, that caused C^2 to change by approximately 0.12.

The effect of interrupting flow at a low C^2 value for a sorbing solute is demonstrated in Figure 3-10, note that all parameter values are identical to those for Figure 3-8, except for the time at which the interruption was initiated. The magnitude of the concentration drop is negligible, compared to that observed in Figure 3-8. At lower C^2 , decreases in solution concentration resulting from sorbed species are negated by an increase in concentration resulting from the resumption of longitudinal diffusion during the resumption period. The magnitude of the drop observed at low C^2 is such that it could not easily be observed from the manner typical to experimental data.

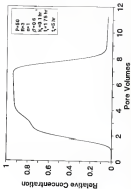


Figure 3-10 RTD shape as influenced by flow integration at a low P

Interrupting flow at a higher C^* value, however, may not allow the development of a significant concentration drop when near-equilibrium conditions exist. For such systems, the interruption must be initiated at somewhat lower C^* values to maintain conditions for establishment of the concentration drop. Hence, the opposing effects of the degree of nonequilibrium and of longitudinal diffusion during the upstroke period must be considered in determining the optimal C^* value for interrupting flow interruptions.

It should be noted that the interruption can also be initiated in the initial portion of the HIC. In this case, no increase, rather than a drop, will occur in the effluent concentration when nonequilibrium is present. To optimize the magnitude of this effect, the interruption should occur at lower C^* values. In addition to the single-perturbation, step-wise approach discussed so far, flow variations (periods of decrease as increased flow velocity) and multi-point perturbations (multiple periods of flow interruption or variation) approaches may also be employed.

The profile associated with HIC (non interrupted) is the relatively poor resolution that exists in the regions near $C^* = 0$ and 1. As the C^* value approaches the limiting value of one (or zero) the changes occurring in C^* become very small. Thus, the magnitude of the change is similar to the analytical sensitivity, variation is small. In this case, the point at which C^* actually reaches one (or zero) is indeterminate. As a result of this poor resolution, HICs that appear to have no tailing (i.e. to have reached $C^* = 0$ or 1) may actually have tailing present. An example of a HIC that appears to have reached $C^* = 1$

is shown in Figure 3-11. The actual $\bar{C}^*$ rather than $\bar{C}$ is, of course not known until $y = 1$.

A major advantage of the flow-interruption method is its decreased sensitivity. The interruption period allows the effects of sorption nonequilibrium to become more apparent, thus enhancing the ability to delineate and investigate conditions of sorption nonequilibrium.

Problems may arise when least-squares methods are used to estimate the model parameters for noninterrupted EECs influenced by nonequilibrium. This is a result of two factors: (1) the curve fitting is weighted towards the central portion of the EEC (e.g., $C^* = 0.5$ to 0.9) because the sum of the squares of the deviations to be minimized is taken in the statistical derivation. This portion of the EEC is not so sensitive to nonequilibrium effects as the lower (early breakthrough) and upper (saturation) portions, which are given less weight; (2) the portions of the EEC most sensitive to nonequilibrium are also those portions most difficult to determine experimentally. As a result of these two factors, curve-fitting of non-interrupted EECs can, in some cases, produce ambiguous parameter-value determinations. This is demonstrated in Figure 3-12, where it is seen that different combinations of parameter values can produce similar simulations. The same parameter values used to produce Figure 3-12 were also used to simulate the flow-interrupted EEC shown in Figure 3-11. The presence of the concentration drop in EECs obtained with the flow-interruption method supplies additional "information" on sorption nonequilibrium, thus enabling more reliable determinations of kinetic parameter values.

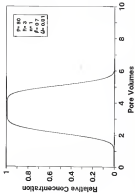


Figure 3-31. Apparent breakthrough to air for a speed of 100 ft/min and a relative humidity of 0.01.

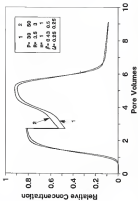


Figure 3-23 Simulated SEC for a set of model polymers, with interruption

Rate-limited sorption reactions are not the only processes that can cause a concentration drop. Transformation reactions (polymerization or chemical) occurring during the interruption period would also result in a reduction in in situ solute concentrations. These reductions would increase the magnitude of the observed drop in effluent concentration and, if not accounted for, would result in erroneous determinations of kinetic parameter values. Therefore, solute losses via processes such as degradation and volatilization must be controlled when readily-degradable or volatile compounds are used.

Physical nonequilibrium

To determine the process(es) responsible for sorption nonequilibrium, the following experimental approach may be taken:

(1) Perform a flow-interruption experiment with a nonreacting solute to determine the presence of physical nonequilibrium. If the BTC exhibits a concentration drop, physical nonequilibrium (i.e., diffusive mass transfer between "mobile" and "immobile" regions) is presumed to be present. Conversely, the absence of a drop signifies the absence of physical nonequilibrium.

(2) Perform flow interruptions with the reacting solute of interest. The presence of a drop in the BTC, in conjunction with the absence of a drop in the BTC of the nonreacting solute, signifies that the nonequilibrium behavior is related to the sorption process. If physical nonequilibrium is present, the kinetic parameters determined for the nonreacting solute may be used to calculate the BTC of the reacting solute. If the BTC is generated well, physical nonequilibrium is

selected as the primary nonspillover mechanism. The presence of an additional unexplained nonspillover mechanism must be presumed however if the RSC is poorly predicted.

(b) Surface film interruption under conditions identical to those in step (1) except with various organic matter partially (or totally) covered. If the magnitude of the drop is reduced (or eliminated) without organic matter is eliminated as the solvent component responsible for sorption nonspillover. In this case, some type of rate-limited surface-organic matter interaction would apparently be the cause of the sorption nonspillover. For HOCs this interaction is most likely intra-organic matter diffusion. Conversely rate-limited interaction between the sorbate and the mineral component is suggested as the mechanism responsible for nonspillover if the magnitude of the drop remains unchanged or increases upon removal of organic matter.

(c) Perform a column experiment without film interruption to determine the significance of film diffusion. The kinetic parameters obtained from step (2), which represent the contributions of all nonspillover mechanisms except film diffusion, are used to simulate the non-interrupted RSC. If the fit is good, film diffusion is insignificant. This step may not be required, however, as film diffusion is generally insignificant relative to intra-organic diffusion for many systems of interest (Guenther and Rhee, 1973; Han, 1973; Edwards et al., 1980; Galloway, 1980; Roberts et al., 1980).

Application of the Method

The application of the Chromatographic method is illustrated with unpublished experimental data of Lee and Seeliger (1979) who observed HPLC from molecular displacement of tritiated water on a nonadsorbed column and the retention 1.5-2 min on an adsorbed column (Lee has a reliability of 440 ng/g HPLC (Chromatogram, 1982) $\pm \log R_{\text{rel}}$ of 2.81 (HPLC Chromatogram, 1983), and a pK_a of 3.66 (Worthing, 1981) HPLC for these solutes were obtained for displacement through water-saturated columns of Butic and Valerol ester. Analytical determination of ^3H and ^{14}C activity in the effluent solution fractions was accomplished using liquid scintillation counting. Experimental techniques were similar to those employed by Lee et al. (1979).

The HPLC from displacement of tritiated water through the Butic column is shown in Figure 3-10. Flow was interrupted at $t^* = 0.15$ min. that communication changes resulting from molecular diffusion were likely to be insignificant. From the absence of a dip in the HPLC, which suggests that physical nonpartitioning was not present. Absence of mobile-molecule retention regions can be expected for this system. Clearly well, peaks also have less than 1 min, retention (retention). The HPLC for displacement of 1.5-2 min through the Butic column, however, does exhibit a significant dip (Figure 3-11). The combination of Figures 3-10 and 3-11 suggests the existence of a sorption-related nonpartitioning mechanism. A HPLC for 1.5-2 min was also obtained (Figure 3-12) for a column packed with Butic oil that had been treated with hydrogen peroxide (H_2O_2) to partially remove organic matter (organic matter content reduced from 0.144 to less than 0.04).

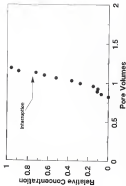


Figure 2-18 Effect of film deformation on reduced water, Beakle and

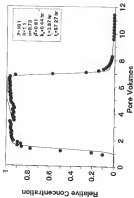


Figure 3-26

Effect of fine-filtration on the pH for 2.4-0. pH 10.0 and 10.0
 with hydrogen peroxide. t_0 = time of adsorption, t_p = time at which pH
 was reached

Comparing Figures 3-13 and 3-14, a substantial decrease in the magnitude of the effluent concentrations drop was observed for the experiment involving K_2 -treated Beale cell. From this it may be inferred that the sorptive nonequilibrium mechanism is associated with the contact signals among. Considering the β -form polymeric structure attributed to cell signals earlier in §. Thus (1978; Turnbull et al., 1980), the nonequilibrium mechanism may involve intra-organic matter diffusion. This hypothesis was also proposed by Khan (1977), who attributed the kinetic sorption behavior exhibited by L.A-2 to the diffusion of acetone from the external surface into the interior of the beads and carbon.

The FFCs obtained by the one-site sorption model using values for the kinetic parameters obtained by this optimization, are also shown in Figures 3-13 and 3-14. Note that the fit was obtained with K_2 fixed, where K_2 and α values used to calculate K_2 were determined from batch experiments. The fit obtained with the K_2 value optimized was essentially the same as that obtained with K_2 fixed. This supports the validity of using independently-determined K_2 values for simulating column FFC data. The same conclusion has been reached by, among others, Lee et al. (1984).

The FFC for displacement of L.A-2 elutes through a water-saturated column of Beale cell is given in Figure 3-17, along with the simulated FFC.

The K_2 values determined from the model simulations were Beale (water-sat) ~ 0.14 , Beale (carbon) ~ 0.46 , Beale ~ 0.00 . Note that the K_2 value from the experiment employing Beale cell treated with K_2K_3 was higher than that obtained from the experiment using the non-treated

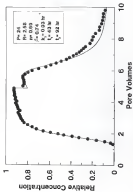


Figure 3-17 Effect of Desorption on BE for I-A-B, solvent cell. t_p = time of breakthrough, t_s = time in steady flow (see text)

Barrett cell. Also note that, comparing the k_d values obtained for the two cells, the Barrett value is smaller. The inverse relationship between exchanger organic-matter content (OC) [defining OCs 1-34], Barrett (0.6 & 34) and k_d is expected given the simplification of mass transfer employed in the 1986 model. The mass transfer coefficient (k_d) can be thought of as a lumped parameter combining several parameters controlling solute mass transfer; among which is diffusive path length. As the diffusive path length increases, the k_d value decreases. The diffusive path length is, in turn, correlated to the quantity of organic matter associated with a surface. Thus, a decrease in k_d is expected for increasing exchanger organic-matter content. Such a relationship has also been observed by Barabekhoff (1980), Barabekhoff and Morris (1981), Walters and Philippot-Ribe (1981), and Jansson and Åke (1984).

Summary

A flow-injection method has been described that should prove to be an effective means of investigating sorption nonequilibrium. Variations of this technique have been used in the past (e.g., Small and Sylvestre, 1982), however, I am not aware of any previous application to the sorption dynamics of organic chemicals. One of the techniques was demonstrated with sorbible displacements of 2-4-b through saturated soil columns. Based upon the experimental results reported herein and elsewhere, the sorption nonequilibrium exhibited by 2,4-b within wet topsoils is expected to be a result of heteroorganic matter diffusion. Experimentally-determined k_d values show an inverse relationship to organic matter content as would be expected.

The flow-interruption technique should prove useful in identifying the presence of nonequilibrium and in evaluating the conditions under which it is important. The method should also provide improved determinations of sorption kinetic parameters. In some situations, the technique may be used to assist in the determination of mechanism(s) responsible for sorption nonequilibrium. Although the method is indirect, its significance is not lessened, considering the present lack of direct, mechanistic techniques.

In addition to its use as a process-investigation technique, there are several practical application aspects associated with the flow-interruption concept. In sample application involves the restoration of contaminated surfaces by flushing (i.e., continuous removal enhanced by pumping-induced gradients) a technique that has received extensive use. Transport of solute under the high flow rate conditions created by pumping may be influenced by nonequilibrium. If such is the case, the desorption of solute in the groundwater will, after an initial rapid decline, exhibit a long, asymptotic approach to zero. Thus, the time and expense required to completely remove the contaminant(s) may become prohibitive. To enhance the effectiveness and efficiency of flushing, pulse-flushing, rather than continuous pumping, may be employed. When the initial phase of rapid decline in solute concentration is over, pumping would be stopped to allow the aqueous and solid phases to approach equilibrium. Once this is accomplished, pumping would be reinitiated. This cycle would be repeated as many times as necessary. In a similar vein, the pulse-flow approach may

also be applied to work marking, the relatively new technique developed
to measure relative distances from the workpiece.

CHAPTER 2 IMPORTANCE OF SURFACE METAPATHOGENS

Influence of Surface-Related Processes on Surface Kinetics

Introduction

As discussed earlier, surface metapathogenesis may result from chemical metapathogenesis (CM) or interfacial diffusion. Given the nature of SOCs, chemical metapathogenesis is not likely to be an important process (Chen et al., 1999; Kricheldorf, 1991; Brennan and Rao, 1991). Thus, interfacial diffusion may be the predominant metapathogenesis process for SOCs. Interfacial diffusion may be separated into two classes, intraparticle surface diffusion (IPSD) and diffusion into mineral particles (IMD), according to the two general types of reactions. Considering the predominant surface reactions for SOCs, diffusion into mineral particles is not likely to be important under most conditions. This is supported by the work of Laflair (Laflair et al., 1998; Laflair, 1999), who reported that sorption for a large number of particles of inorganic substances was independent of time. This indicated that sorption seemed to be restricted to external surfaces alone and that sorption on internal surfaces, if present, was negligible. Conversely, sorption on organic matter-containing systems exhibited a significant long-time approach to equilibrium. Earlier

behavior has been reported by Hugg (1970), Hugg and others (1966), Meyer et al. (1971), Williams et al. (1972), and Brown (1974).

Interfacial diffusion may, however, be important for other chemical elements. For example, the long-term sorption-desorption behavior exhibited by Flycatcher on these California soils was attributed to diffusive transfer in interfacial regions of the clay structure (Gillman and Meyer, 1977).

Diffusion within the matrix of organic matter has been proposed as a possible mechanism responsible for intra-labeled compounds/biomarkers by several authors (Gardner et al., 1966; Meyer, 1971; Landwehr and Adriaens, 1971; Meyer et al., 1972; Khan, 1973; Lefleur et al., 1973; Bernick and van Haelst, 1974; Hugg and Goring, 1969; Rao and Goring, 1961; Freeman and Goring, 1961; Bostrom and Van der Hor, 1963; Landwehr and Frick, 1966; Hollibaugh and Bernick, 1968; Olson, 1969; Hollibaugh et al., 1969; Rao et al., 1969; Bostrom and Rao, 1969; Ward-Olsen et al., 1969).

Permeating into soil organic matter has been proposed as the primary sorption mechanism for HCEs (Olson et al., 1974; Bernick and van Haelst, 1974; Freeman and Goring, 1961; Gardner, 1964). Soil organic matter may be pictured as a three-dimensional network of randomly oriented polymer chains and as having a relatively open, flexible structure permeated with voids (Hugg and Hopper, 1966; Khan, 1973; Robinson, 1979; Bernick, 1980). Such materials in soils are pictured as amorphous-like aggregates in a model proposed by Gardner (1964). With such a "porous" structure attributed to organic matter, the existence of an intramatrix sorption-diffusion process is definitely possible. If

complex nonequilibrium is caused by 1288. The structural nature of the existing chemical should influence the kinetic behavior. This question is investigated in this section.

Kinetics and Mechanism

The literature was searched for data on the nonequilibrium sorption of organic compounds by soils, sediments, and aquatic materials. Values for the partition coefficient (K_p) and the sorption rate coefficient (k_p) were desired. To facilitate data analysis, the linear free-energy relationship (LFER) technique was employed. This correlation analysis technique is widely used in chemistry to evaluate relationships between equilibrium constants and/or rate constants. If a linear relationship occurs when the logarithm of the rate constants of a series of compounds are plotted against the logarithm of their associated equilibrium constants, a LFER is said to exist (Bentley, 1978).

All of the data were obtained with one of three experimental techniques: batch sorption rate, gas-purge desorption, or desorbable displacement. With one exception, the sorption data collected with the batch-type and the gas-purge techniques had been analyzed with the use of a kinetic model. In these cases, the appropriate values of k_p and k_d reported by the source authors were used for this study. Oliver (1985) presented batch-rate data and reported the time to reach 50% of complete desorption (t_{50}). For this data, a first-order rate constant (k_d) was calculated as $2.405/t_{50}$.

Since the details of the data from the various experiments had not been quantitatively analyzed. In these cases, a mathematical model was employed to determine the appropriate sorption nonequilibrium parameters. The nonlinear least-squares optimization program OPTIM (van Gemmen, 1981) was used to fit the model to measured breakthrough curves (BTCs) to determine values for the sorption parameters.

The organic chemicals for which sorption data were compiled fall into two general classes: hydrophobic organic chemicals (HOCs) and nonhydrophobic organic chemicals (NHOCs). HOCs are those whose sorption is considered to be predominated by hydrophobic sorption. Hydrophobic sorption is generally characterized by linear, reversible, and singular isotherms, and is controlled primarily by carbon organic matter because of their more reactive nature. NHOCs are prone to specific sorption reactions.

The point K_p and K_d values used for the analyses presented herein are listed in Tables 4-1 and 4-2. The data are divided into two types: HOCs (Type I, see Table 4-1) and NHOCs (Type II, see Table 4-1). Notations regarding the type of experiment used, whether the data were simulated by the source authors or by the current author, and the source citation are provided.

Results and Discussion

Preliminary analysis of data

Identification of mechanisms responsible for sorption nonequilibrium is not possible by curve-fitting of experimental data with models alone. It is important to evaluate the nature of the system

Table 4-1 Literature values for k_1 and E_a (Type 1 Chemistry)

k_1 (s ⁻¹ /g)	k_1 (s ⁻¹)	Chemical	Exp. Tech.	Simulation	Reference
7300	6.1×10^{-3}	benzothienobenzene	CP	SA	Kutskheff and Morris, 1982
1350	0.05	benzothienobenzene	CP	SA	"
1350	0.26	benzothienobenzene	CP	SA	"
33000	1.1×10^{-3}	benzothienobenzene	CP	SA	"
28000	1.2×10^{-3}	benzothienobenzene	CP	SA	"
3400	0.01	benzothienobenzene	CP	SA	"
2300	0.03	benzothienobenzene	CP	SA	"
3400	1.4×10^{-3}	benzothienobenzene	CP	SA	"
8100	3.2×10^{-3}	pentachlorobenzene	CP	SA	"
7100	6.7×10^{-3}	pentachlorobenzene	CP	SA	"
1900	0.01	pentachlorobenzene	CP	SA	"
3100	6.1×10^{-3}	pyrene	CP	SA	"
1300	0.03	pyrene	CP	SA	"
120	0.3	trifluoride	CP	SA	"
21	0.01	trifluoride	CP	SA	"
850	6.2×10^{-3}	trifluoride	CP	SA	"
1450	6.4×10^{-3}	diacetylene	S	SA	Waters, 1981
13000	3.7×10^{-3}	dichlorodiphenyl	CP	SA	Conner and Elmer, 1984
11000	8.8×10^{-3}	nitrochlorophenyl	CP	SA	"
170000	3.3×10^{-3}	benzochlorophenyl	CP	SA	"
34000	7.3×10^{-3}	benzochlorophenyl	CP	SA	Slone, 1983
130000	7.5×10^{-3}	benzochlorobenzene	CP	SA	"
1500	0.05	pyrene	CP	SA	Kutskheff, 1988
200	0.14	phenanthrene	CP	SA	"
80	0.13	naphthalene	CP	SA	"
8.5	0.06	naphthalene	CP	SA	"
24	0.48	naphthalene	CP	SA	"
1230	0.08	1,2,3,4-			Ma and Gschwend, 1991
		trifluorobenzene	CP	SA	
1280	0.08	1,2,3,4-			
		trifluorobenzene	CP	SA	"
1.0	1.50	benzene	CP	SA	Chapter 3
13	0.06	chlorobenzene	CP	SA	Chen 1993
31	0.42	1, 2-dichlorobenzene	CP	SA	"
34	0.30	1, 2, 4-			
		trichlorobenzene	CP	SA	"

Table 4-5 (Cont.)

R_D (wt-%)	R_A (wt-%)	Material	Exp. Tech.	Simulation	Reference
42.4	0.000	isobutene	0	Pa	Müller and Weber 1986
14.4	0.10	isobutene	C	Pa	
7	0.10	1,2,3-			Southworth et al., 1987
		isobutene	C	Pa	Southworth
10	0.11	1,2,3,4-			et al., 1987
		isobutene	C	Pa	
0.1	4.3	isobutene	C	Pa	Lee et al., 1988
0.14	0.0	isobutene	C	Pa	"
0.30	0.7	isobutene	C	Pa	"
0.41	0.8	isobutene	C	Pa	"
3.34	0.44	isobutene	C	Pa	Wood et al., 1987
1.45	1.01	isobutene	C	Pa	"
0.44	0.11	isobutene	C	Pa	"
0.14	0.40	isobutene	C	Pa	"
0.14	1.04	isobutene	C	Pa	"
1.00	0.10	isobutene	C	Pa	"
0.50	0.70	isobutene	C	Pa	"
0.10	1.70	isobutene	C	Pa	"
0.04	1.70	isobutene	C	Pa	Angley, 1988
0.10	1.10	isobutene	C	Pa	"
0.04	4.10	isobutene	C	Pa	"
0.17	4.10	isobutene	C	Pa	"
0.10	4.70	isobutene	C	Pa	"
0.10	4.80	isobutene	C	Pa	"
0.14	1.70	isobutene	C	Pa	"
0.10	4.70	isobutene	C	Pa	"
0.04	1.00	isobutene	C	Pa	"
0.14	1.04	isobutene	C	Pa	"
0.10	1.00	isobutene	C	Pa	"

0 = isobutene, GP = gas-phase-diffusion, C = isobutene, Pa = isobutene, Pa = isobutene

+ = value used in Figure 4-5

av = value used in Figure 4-5

|| = average of three (or duplicate) used for Figure 4-5

* = analysis did not at 100°C

Table 4-2. Literature values for k_p and $k_p/k_t^{1/2}$ (Cyan 12 Oxidation)

k_p ml/g ²	k_p (hr ⁻¹)	pH	Monomer	Exp. Temp.	Classification	Reference
1.46	2.1×10^{-2}	3.4	2,4-di-oxian	0	SA	Bar et al., 1979
2.08	0.00	2.5	2,4-di-oxian	C	SA	"
0.86	5.4×10^{-3}	2.4	acrylonitrile	0	SA	"
0.13	0.00	2.3	pieloxan	0	SA	Wolfe, and Agin, 1983
0.7	0.00	4.1	pieloxan	4	SA	"
0.4	9×10^{-3}	0.3	pieloxan	4	SA	"
0.54	0.015	4.0	pieloxan	0	SA	"
0.8	0.04	5.0	pieloxan	0	SA	"
1.8	0.04	4.1	pieloxan	0	SA	"
0.46	0.014	0.4	pieloxan	0	SA	"
3.32	7.7×10^{-3}	4.5	acrylonitrile	C	SA	Baron and Elzohy, 1977
0.002	0.00	7.1	pentachlorophenol	0	Pa	Furman and Hildebrand, 1963
0.10	0.01	5.0	pentachlorophenol	C	Pa	Lee, 1980
0.88	15.33	2.0	quinoxaline	0	Pa	same work

0 = batch; C = gas-liquid; T = column

SA = surface catalyst; Pa = pressure catalyst

being investigated is that mechanism which are unlikely to be involved may be identified. With these improbable mechanisms eliminated, the number of probable mechanisms is reduced. In some cases, it may be possible to reduce the number of probable mechanisms such that a single mechanism is determined to be the likely cause of nonequilibrium.

The data and the systems from which they were obtained are evaluated below. The discussion is structured by type of nonequilibrium mechanism in order to facilitate the elimination of improbable mechanisms.

Typical nonequilibrium As discussed by Brannon and Lee (1987), non-working, as well as working, systems should exhibit asymmetrical breakthrough curves when transport-related nonequilibrium (TNE) is present. Among the data sets evaluated, the BTCs of the non-working systems were symmetrical for the data of Angley (1987), Cameron and Kluge (1977), Lee et al. (1984), Miller and Weber (1986), Robinson et al. (1987) Lee et al. (1978) and West et al. (1987). In addition, the particle size of the sorbents used in all these studies was less than 1 mm. It can be readily shown that, for the porosities typical of natural soils and sediments, pore diffusion within particles of this size is fast enough such that TNE will be relatively insignificant. The BTC for the non-working system of Goodworth et al. (1987) exhibits some asymmetry. However, these authors successfully simulated the BTC with the equilibrium adsorption-desorption model, which suggests that any TNE that might have been present was relatively insignificant. The particle size of the sorbents used for the batch and gas-phase experiments were, in all cases, less than or equal to 1 mm.

Based on the discussion above, it can be concluded that TOE was either non-existent or of negligible importance for all of the data utilized herein. Hence, TOE may be eliminated as a potential nonequilibrium mechanism for these data. The validity of this conclusion will be evaluated in light of the discussions presented below.

Chemical nonequilibrium Because of their chemical structure, MOCs are generally not affected by TOE. Thus, TOE may be tentatively regarded as an inequitable nonequilibrium mechanism. The validity of this hypothesis will be evaluated in light of the discussions presented below. As opposed to MOCs, OMOCs can be significantly influenced by TOE. The literature is replete with investigations of specific interactions between these types of chemicals and soils and sediments.

Intramolecular diffusion Considering the nature and sorptive behavior of MOCs (e.g., sorption predominated by organic matter, water immiscibility sorption for polar surfactants), TOE is a likely potential nonequilibrium mechanism. As previously mentioned, TOE has been proposed as a possible nonequilibrium mechanism by several researchers collectively. TOE is an unlikely mechanism also because of the reasons above. Thus TOE is unimportant for MOCs is supported by data showing the sorption kinetics of MOCs to be rate-limited for surfactants consisting organic matter and not rate-limited for mineral surfaces. Data exhibiting this type of behavior have been reported by several authors (Nagai et al., 1975; Morris and Barron, 1976; Neper et al., 1971; Salomons et al., 1972; Brown, 1974; Laflamme et al., 1978; Laflamme, 1979, 80).

LDS may be a possible sorption mechanism for BBOs as well as for BOCs. In addition, LDS is also a possible mechanism for BBOB.

Based on the discussions above, the following mechanisms may be considered as the most probable potential causes of sorption nonequilibrium for the analyzed data: (i) BOCs— intramorphic surface diffusion; (ii) BBOBs— chemical nonequilibrium and intramorphic diffusion.

Data analysis

The data in Tables 4-1 and 4-2 are presented in Figure 4-1. Three features of the plot are readily apparent. First, the data segregate into two distinct regions according to the chemical nature of the sorbates ($\alpha = 1$, BBOs and BBOBs). Second, the data exhibit an inverse relationship between k_p and E_p . Third, the relationships are log-log linear, validating the LFR approach. We will first discuss the sorption factors, returning thereafter to the first.

Relationship between k_p and E_p . For LDS sorption nonequilibrium is the result of nonuniform mass transfer of sorbate from the exterior surface of the organic matrix into the interior matrix. Such diffusional mass transfer is a function of three factors: (i) the diffusivity of the diffusing species; (ii) the mechanism of diffusion associated with the sorbate matrix; and (iii) the diffusion path length. For BOCs, E_p is influenced gravimetrically by two components, E_{in} (partition coefficient normalized to organic matrix) and E_{out} (activation of organic matrix). E_{in} and diffusivity are both functions of the size and physicochemical nature of the solute and are therefore related, also E_{out} and diffusion path length are related. Since the inverse

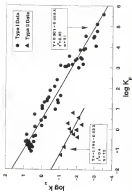


Figure 3-4 Relationship between sorption rate constant (K_p) and equilibrium sorption constant (K_d)

relationship between k_1 and k_2 observed in Figure 4-1 is expected for the case of TDB-induced nonequilibrium. An inverse relationship between k_1 and k_2 has also been observed by Brinson and Rao (1980), Barickhoff (1980), Barickhoff and Morris (1981), and Kashi-Karna et al. (1981).

As discussed above, TDB was delineated as the only probable nonequilibrium mechanism for the BPO data analyzed. This, in combination with the inverse relationship discussed above, is strong evidence for the existence of TDB and for it being the cause of the nonequilibrium exhibited by the BPO data. To further test the validity of this hypothesis, subsets of the BPO data presented in Table 4-1 were analyzed.

Data for a homologous series of chlorinated benzenes are presented in Figure 4-2 (the data used in Figure 4-2 are listed in Table 4-1). A difference of three and one half orders-of-magnitude exists between the k_1 values of benzene and hexachlorobenzene (HCB). The magnitude of this difference may be compared to that expected for the case of TDB-induced nonequilibrium. As mentioned above, TDB is a pore-diffusion process since the pore diffusion coefficient (D) is influenced by the size of the diffusing molecule, benzene and HCB would be expected to have different D values. The mass transfer coefficient (k) for the TDB model is related to the pore-diffusion coefficient by the following equation (Brinson and Rao, 1980 and references cited within)

$$k = (1/2) D_0 / (V \delta^2) \quad (4-1)$$

where α is a shape coefficient, V is porosity, δ is the characteristic diffusion half length (μ), D_0 is diffusion coefficient in bulk water

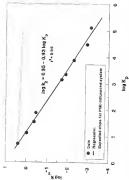


Figure 4.2. LMS for a series of chlorinated, the data used are indicated in Table 4.1

(U^2/T) , and $U = (h_0/T)$. Hence, the influence of the size of the solute on U can be directly related to an effect on α . For α given constant (k , μ , d , ϵ , and T constant), the differences in α values for different solutes would only give differences in h_0 values. Therefore, the differences in the α values for benzene and BzB can be evaluated by comparing their respective h_0 values.

The h_0 values for benzene and BzB, calculated with the Debye and Laidler correlation (1994) are plotted in Figure 4-4. Even though the values are scaled to the scaling reference values and that a line is used in place of the point values to facilitate comparison, it is obvious that the slope exhibited by the data is much greater than that expected for a system influenced only by TSE. Thus, the magnitude of the slope is, of itself, support for the existence of TSE.

Note that the data in Figure 4-4 include five different solvents. The high correlation ($r^2 = 0.99$) between h_0 and h_0^* suggests that the nature of the organic solvent has negligible influence on the rate-limited process. This type of behavior would not be expected for a system influenced by TSE where the nature of the solvent would be expected to be of greater significance. This type of behavior would be expected, however, for a system involving a physical process such as TSE. Thus, the data presented in Figure 4-4 support the improbability of TSE and the existence of TSE.

Data for a homologous series of polynuclear aromatic hydrocarbons (PAHs) are presented in Figure 4-5 (the data used in Figure 4-3 are noted in Table 4-1). The slope exhibited by the PAH data is much greater than the slope that would result from a TSE-controlled system,

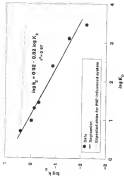


Figure 4-3. Log for a series of polymeric systems, the data used are indicated in Table 4.1

at the same time for the chlorinated benzene homologous series. The data in Figures 4-3 represent the different evidence as for the chlorinated benzene data, the high correlation ($r^2 = 0.71$) supports the hypothesis of GHS involvement.

The slope and intercept values for the chlorinated benzene series and the HCB series are essentially identical. The fact that two series of values of different chemical series exhibit identical behavior is suggestive of a physical process. Such behavior would not be expected for GHS-influenced systems. Given the discussion above, the relevance of GHS is strongly supported by the data presented in Figures 4-3 and 4-4.

Sensitivity analysis of the k_1 , α , k_2 relationship The inverse relationship between $\log k_1$ and $\log k_2$ exhibited in Figure 4-1 can be quantified with linear regression analysis. The procedure most commonly employed, based on the least-squares model, assumes that the independent variable has no associated error ($\sigma = 0$, is known absolutely). This assumption is invalid in our case since measured values of k_2 do have an associated error. Hence, the analytical procedure must account for uncertainty in the independent, as well as the dependent, variable. Such a technique, called the generalized least functional (GLF) regression method, was discussed by Bullock (1985). The GLF regression minimizes the sum of the products of the vertical and horizontal deviations of each point from the line, whereas the common regression minimizes the sum of the squares of the vertical deviations.

The following regression equation relating $\log k_1$ and $\log k_2$ for the Type-1 data was found with the GLF method:

$$\log k_p = 8.508 - 0.444 \log K_p \quad (r^2 = 0.99) \quad (4-3)$$

the correlation exhibited by the Type-I data is remarkable, especially considering that the data were obtained by many investigators and with different experimental techniques.

Equation 4-2 should prove useful as an empirical relation to provide first-approximation type estimates of k_p values for RO_2 - Al , that would be required to estimate k_p (or α value for K_p) which can be obtained from a bench experiment or from knowledge of solute properties (solubility, K_{ow} , molecular size, etc.) and the organic surface content of the surface (e.g., DeJoa et al., 1979; Kuehnhold et al., 1979; Sahji et al., 1987). This provides the capability to evaluate the nonequilibrium-adsorption potential of a given species (i.e., organic, inorganic, solvent, solute). Such information would be useful in the selection of appropriate solute transport models (i.e., equilibrium vs. nonequilibrium), in the planning and evaluation of risk/benefit restoration schemes, and in the management of surface water contamination.

Equation 4-3 also provides a means to independently determine values for the sorption kinetic term(s) in transport models that include sorption nonequilibrium. This, in combination with independent estimates for dispersion and retardation factor values (see above), would allow one an attempt to synthesize nonequilibrium-affected RTGs.

Although a regression line is shown in Figure 4-2 for the Type II data, it is obvious that the correlation is relatively poor ($r^2=0.4$). The poor correlation is likely the result of the small range in K_p values for the Type II data set and also the fact that half of the data are for a single compound.

Influence of chemical nature of solute on kinetic behavior as noted above. It is readily apparent that the data in Figures 4-6 clustered in two distinct groups according to chemical type. The k_2 values for the Type II solute are approximately one-order-of-magnitude smaller than those of the Type I solute. Thus, the Type II chemicals appear to be influenced by another rate-limiting mechanism, instead of, or in addition to, the SN2 mechanism affecting the Type I chemicals. Considering the nature of the chemicals comprising the Type II group (chemicals of high polarity, presence of reactive functional groups), this observation is not unexpected. Specific interactions between functional groups of organic solute and specific solvation of these solutes are possible. In fact, it has been suggested that specific chemical interactions can occur between functional groups of soil organic matter and the triazine herbicide atrazine (Beyan, 1972; Li and Foltz, 1973), the carboxylic acid herbicide picloram (Shawish, 1977), and chlorophenols (Gray, 1972; Gray and Russell, 1981). Thus, the sorption nonequilibrium exhibited by the Type II chemicals may be the result of CHE or a combination of CHE and SN2.

The influence of the chemical nature of the solute molecule on the kinetics of interaction with organic matter can be further evaluated by analyzing the effect of changes in pH on the sorption kinetics of ionizable chemicals. Sorption of acidic chemicals, such as picloram (1,4-B), and pentachlorophenol (PCP) is controlled by the ionization state when pH is lower than their pK_a (Bailey et al., 1964; Lee et al., 1980). Therefore, these chemicals will generally behave as SN2 under these conditions. For example, based on experimental results, physical

absorption (Cl^- , hydrophobic organic) has been suggested as the primary sorption mechanism under low pH conditions (pH lower than pH_a) for 2,4-D (Kuo, 1973, 1974), picloram (Gougeon, 1978; Bailey et al., 1984), and PPT (Lee et al., 1988). Sorption rate constants for these ionizable compounds would be expected to fall near the Type I group when their behavior is controlled by the molecular form Cl^- , when the pH is lower than the pH_a . Conversely, rate constants obtained in systems with pH values much greater than pH_a would be expected to fall within the Type II group.

Sorption rate constants for pentachlorophenol ($\text{pH}_a = 4.75$ (Kuo, 1987)) at two different pH levels (Tables 4-5), one below the pH_a and the other much larger, are plotted in Figure 4a. For comparison, the regression equations obtained for the data presented in Tables 4-5 and 4-6 are also shown. The rate constant obtained under low pH conditions fall near the Type I group as expected. Also as expected, the rate constants obtained under high pH conditions lie within the Type II group. The k_d values for ionizable chemicals such as these would be expected to be influenced by the degree of ionization and, hence, to depend upon the pH_a - pH relationship.

It should be noted that the experiment reported by Furutani and Linklater (1987) was performed with a very low ionic strength. For organic acids such as pentachlorophenol, the magnitude of the ionic strength may be expected to influence their sorption dynamics. In fact, Lee (1989) observed the sorption-desorption behavior of pentachlorophenol in a high pH, relatively high ionic strength (20 mM sodium) system to follow that of the Type I group. This was attributed to the formation

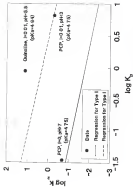


Figure 4-4 Effect of pH on molecular speciation and the relationship between K_p and K_a .

of metal cations/phosphorus ion pairs. The behavior exhibited in Figure 4a is strong evidence that the Type I chemicals are influenced only by 100μ , whereas the Type II chemicals are influenced by 500 or by 200 and 1000 .

The nature of the specific interaction between a RBC and a given nutrient is dependent upon the nature of the nutrient and of the nutrient, given the wide range in physicochemical properties exhibited by RBCs. The complex behavior of this class of chemicals is expected to vary widely. In particular, it is expected that k_1 values for RBCs would be dependent upon the nature of specific nutrient-nutrient interactions. The k_1 values for RBCs might be expected, therefore, to exhibit greater variation in comparison to those for RBCs. In such, it is more likely that Type II chemicals would exhibit a series of roughly parallel LFRs, rather than a single one as is shown in Figures 4a) and 4b. The relative positions of the LFRs (i.e., the intercept values) would, of course, be dependent upon the nature of the specific nutrient-nutrient interactions. The intercept value of the LFR reflects the degree to which the nutrient dynamics of a series of chemicals is constrained and would, therefore, be indicative of the specific-interaction potential of the system. The smaller the specific-interaction potential of a RBC group, the closer the associated LFR would be to that of the RBCs. The relative position of k_1 values for Type II chemicals limits the discussion in this paragraph to nutrient specialization. Additional data are required to substantiate the postulated behavior.

So far, the behavior of nutrient specific species (RBCs) has not been discussed. Although no data were found for such chemicals, it

might be anticipated, based upon data known about various exchange reactions, that k_2 values for H_2O would be larger than those for H_2O_2 (i.e., the LPH for H_2O would plot above the H_2O_2 LPH). Ion-exchange has been demonstrated to be an instantaneous physical process involving no chemical bond formation (e.g., Helfferich (1942)). Therefore, ion diffusion within the exchange rather than the actual exchange "reaction" itself, may be considered as the rate-limiting step for ion exchange (Helfferich, 1942). Considering the nature of soil organic matter, it is likely that a relatively large proportion of cation exchange sites associated with organic matter are located near the soil/solution interface. Furthermore, based on the double layer theory, it may be anticipated that the electrostatic requirements for ion exchange can be satisfied by ions residing within the electrical field of the surface. As a result, the effective diffusion path length for H_2O might be expected to be shorter than that for H_2O_2 . The k_2 values for H_2O would therefore be larger, since k_2 is a function, in part, of the diffusion path length. Because of the nature of cation exchange and the conformation of organic matter, as described above, the ion exchange of cations on organic matter may be considered as essentially a diffusion process. In other words, any rate-limited behavior exhibited in such systems may usually be attributed to film diffusion. This is supported by the work presented by Boudi Ghoul, 1984. Boudi et al (1984). They investigated the kinetics of ion exchange of metal cations on humic acids and peat and concluded that the rate-limiting step was film diffusion. More research on H_2O and H_2O_2 is required to further elucidate what has been discussed above.

A preliminary investigation of the behavior of GGE was performed using sphulonic acid organic base. The values for k_p and K_p obtained from the experiments are plotted in log-form in Figure 4-4. (The column and methods employed were the same as those described in Chapter 3, and the apparatus for a listing of the raw RTG data). It appears that sphulonic, which at the given pH is approximately 98% ionized, exhibits a lesser degree of rate-limited behavior, in comparison to the Type I group. This is suggested to arise from the behavior of the ionized species, considering that cation exchange is expected to have a smaller characteristic time of reaction in comparison to that of irreversible adsorption onto ion-exchange sites.

The difference in kinetic behavior between ionized and unionized species was further investigated using cesium. A cationic displacement experiment for the isotopic exchange of ^{137}Cs on bentonite was performed in the manner described in Chapter 3. Properties of the column (e.g., bedlet number, length) were similar to the column used for the RTG.

The RTG obtained for ^{137}Cs is shown in Figure 4-5 along with the RTG for ^{137}Cs and sphulonic acid. Note that the x-axis is scaled to relative pore volume ($t = t_p/\tau_p$) to facilitate comparison of relative ionized behavior. It is apparent that while ^{137}Cs exhibits some ionized behavior (a slight tail), this ionizability is much less than that exhibited by sphulonic acid. In other words, the sorption of sphulonic acid was rate-limited ($t = t_p$, rate-limited) than is that of cesium. This behavior is readily resolved using the explanation discussed above: the characteristic time of reaction associated with

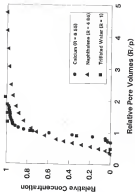


Figure 9-1: Comparison of osmotic behavior, anti-a-Burke

cation exchange of ^{90}Sr is much smaller in comparison to that associated with the sorption of nepheline, which is suggested to involve diffusion mass transfer within the solid organic matter. The relatively rapid rate of ion exchange of metal cations in organic matter was also reported by Burni et al. (1981). Both behaviors, where the cation (^{90}Sr) exhibited a lesser degree of nonequilibrium than did the BOCs, was also observed by Muel-Stein et al. (1988).

The influence of molecular attraction of the cations on sorption kinetics was further evaluated by performing a series of chloride displacement experiments for several homologous series of BOCs, the cation and methods employed were those described in Chapter 5. Raw data for the BOCs are provided in the appendix.

The log values of k_d and k_p for three homologous series are plotted in Figures 4-6. It is apparent that each series is described by a slightly different LFER. However, the differences are so slight that one global LFER can describe all the data with $(\log k_d = 2.81 + 2.31 \log K_p, r^2 = 0.94)$. This suggests that differences in behavior resulting from differences in the chemical nature of the three series are of relatively minor importance. This supports the hypothesis that a physical process, such as interfacial diffusive mass transfer, controls the rate-limited behavior of these BOCs.

The influence of substitution groups on trace-limited sorption was investigated using several alkylenes. The unsubstituted benzene, naphthalene, anthracene series was used to establish the basic relationship between k_d and K_p (see Figure 4-11). The influence of a single-carbon function group (i.e., methyl) was evaluated using the

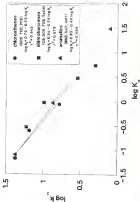
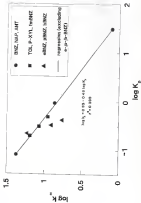


Figure 4-4

[illegible]

series (Table I) is a relatively narrow series. It appears that the presence of the functional group does not affect the nature of the $k_1 - k_2$ relationship (see Figure 4-7). The influence of side-chain halogen group was evaluated using the ethylenic monosubstituted, α -haloethylenic series. It appears that the presence of a chain of three to four carbons affects the $k_1 - k_2$ relationship. For a process involving diffusion within an organic polymer, this behavior may be explained as resulting from the additional resistance to diffusion that exists for the halogen entering. In other words, the presence of the ethyl chain hinders the diffusional mass transfer of α -propylene and α -butylene. The influence of molecular structure on diffusion in polymers has been investigated in the field of polymer physics.

Summary

The influence of the chemical nature of the organic molecule on the rate of the interaction with natural substances was investigated. Strong evidence exists and is presented for the existence of the heterogeneous nature diffusion process and this is being the cause of the complex non-equilibrium exhibited by the ROC data analyzed. An equation was presented that may be used to calculate approximate values of the sorption rate constant for ROCs. This provides a means to evaluate non-equilibrium potential and to attempt to predict non-equilibrium behavior. Evidence was also presented that suggested that ROCs may be influenced by some combination of two non-equilibrium mechanisms, classical non-equilibrium and heterogeneous nature diffusion. It thus appears that, in any case, the sorption kinetics of organic molecules

is controlled by interfacial phenomena between the surface and the aqueous phase as the surface.

Such processes could have several important effects, such as reducing the effective travel time of a solute, increasing the time required to "flush" a contaminated aquifer, causing the biodegradability observed in many sorption experiments, and being responsible for the formation of so-called "bound residues".

The sorption kinetics of pesticides chemically appears to be significantly influenced by pH. Additional work is required to explore this relationship.

Influence of Organic Constituents on Sorption Kinetics

Introduction

The influence of organic constituents on the sorption and transport of hydrophobic organic chemicals (HOCs) in soils and groundwater has become an active area of research. The impact of constituents on phase distribution (e.g., solubility, sorption) of HOCs has been the major focus of attention. For example, Galloway et al. (1982) found the solubility of HOCs in polar solvents to increase in a log-linear manner with increasing volume fraction of surfactant (C_{sf}) in a binary mixture. The log-linear model has since been found to generally be a good description of the influence of surfactant upon the solubility of HOCs (Bos and Lepp, 1989; Harris et al., 1989; Galloway and Hansen, 1991).

A model describing the effect of surfactant upon the sorption of HOCs was presented by Bos et al. (1989). The relationship between the equilibrium sorption constant (K_d) and C_{sf} was of the form

$$\log K_{eq} = x + \frac{r}{n} + d$$

(4-5)

where K_{eq} is the sorption equilibrium constant for the mixed-solvent system with values of vol. g^{-1} in eq 4-5; $x = \log a$ where a represents the continuity power of the continuous expressed via the slope of the SEC solubilizability profile; n is an empirical constant that represents any deviation of the sorption- K_{eq} functionality from that observed for crystalline and $d = \log K_{eq}$ where K_{eq} is the equilibrium constant for sorption from water. The model has been shown to be valid for both sorption (Shack-Klein et al., 1980, 1981, 82 and 1983; 1986a) and transport (Shack-Klein et al., 1983) of HCs.

The influence of cosolvents on the kinetics of sorption of HCs, however, has received very little attention. Shack-Klein et al. (1987) observed a decrease in the asymmetry of breakthrough curves (BECs) with increasing fractions of cosolvent (C₂) for displacement of the hydrophobic dyes and organics through a porous cell column. The relationship between BEC asymmetry, which was attributed by the authors to sorption, desorption, and K_{eq} suggests that the rate of sorption is greater in the presence of a cosolvent. Shack-Klein et al. (1987, 1988) suggested that the influence of cosolvent on interactions between the solute and solvent organic matter was responsible for the observed behavior. Williams and Delonghi-Hill (1989) reported that sorption equilibrium of dyes by soils from water/ethanol mixtures was attained in shorter times with higher K_{eq} .

The limited amount of work that has been done on the influence of cosolvents on the rate of sorption of HCs has been qualitative in nature. To investigate and evaluate the relationship between sorption

and, conversely, a quantitative analysis is required. The work presented herein is an attempt to provide such an analysis.

Summary

The impact of organic molecules on the equilibrium sorption of RBCs is well established, as discussed above. The presence of surfactant appears to also have an impact on the rate of sorption. The existence of a relationship between these two phenomena, and the nature of the relationship if one exists, are the central questions to be investigated herein. The critical component to any such relationship would be the existence of a relationship between the sorption rate constant (k_2) and K_2 . Such a relationship was presented earlier in Chapter 4, where k_2 was shown to be a log-log linear inverse function of K_2 .

$$\log k_2 = a \log K_2 + b \quad (4-4)$$

with $a = -0.468$, $b = 0.394$, and $r^2 = 0.91$. In eq 4-4, k_2 has units of hr^{-1} and K_2 has units of ml g^{-1} . Rate-limited intercalation between surfactant organic matter and the carbon, involving diffusion into/transfer within the organic matter matrix, has postulated as being responsible for the observed relationship.

A model describing the influence of surfactants on the rate of sorption of RBCs may be developed by coupling the relationships that have been previously reported between k_2 and K_2 , and between K_2 and K_1 . Note that the units for K_2 in eq 4-4 and 4-6 differ. To attain equivalency, eq 4-6 may be rewritten as

$$\log k_2 = a \log K_2 + b' \quad (4-5)$$

where $k' = k + a \log \Phi$, Φ is the volume fraction of CH_2Cl_2 , a is the solvent and k_0 is the value of k and g^{-1} .

Substitution of eq 4-4 into eq 4-3 results in the following

$$\log k_0 = \beta \log k + a \quad (4-5)$$

where k_0 is the capture rate constant ($\text{dm}^3/\text{mole} \cdot \text{sec}$) for the mixed-solvent system; $\beta = a/(1+a)$ and $a = a/k'$. Note that $a = \log k_{\text{hom}}$ where k_{hom} is the rate constant for capture in aqueous systems.

A log-linear functionality between k_0 and k is expected for RDS based on eq 4-4. Both an experimentally-determined relationship for k_0 versus k could be manipulated to estimate a k_0 value for an aqueous system. If the functionality between k_0 and k_0 were to hold for mixed-solvent systems, the regression equation they represent should be applicable for both aqueous and mixed-solvent systems. Values for k_0 in mixed-solvent systems could then be calculated independently.

Materials and Methods

Kinetic displacement experiments were performed with naphthalene using columns packed with a sandy soil (Benton fine sand, organic carbon content (OC) = 0.3%)¹⁴. The experimental apparatus and methodology were similar to those employed by Mack-Elliott et al.¹⁴ (1987) and Lee et al.¹⁵ (1988). RDS for phenanthrene, naphthalene, and fluorene, obtained by kinetic displacement with mixtures of water and acetone through column packed with Benton soil (OC = 0.3%) as reported by Mack et al.¹⁴ (1987), were used as an additional source of data. A fluorescence probe, where sorption is assumed to occur at both an equilibrium state and a first-order domain, was used to elucidate the measured RDS. A

nonlinear least-squares optimization program (GSTER from Cray Research [19]) was utilized to determine values for the ten characteristic nonequilibrium parameters contained in the model: β the fraction of instantaneous sorption; and α the Damkohler number (the ratio of residence time to characteristic time of sorption) which is more accurate k_p values for all other model parameters were obtained from independent sources. Porosity number (1.0), diffusivity, k_d from the ETC of isolated water, a sorption delay distribution factor (2), which contains k_p , from the absolute normalized first temporal moment of the sorption-elution ETC (4.1, Yeh and Cussler, 1981); and pulse width (2) from the experiment itself. Estimated values for k_p and k_d were employed to evaluate the validity of eq 4-6.

Results and Discussion

Validation of Model

The ETCs for sorption in square columns ($L_c = 0$) and binary mixtures ($L_c = 0.1, 0.2$, and 0.3) are presented in Figures 4-4. Parameter values for the three-column model simulations are given in Table 4-2. The leftmost displacement of the ETCs ($L_c = 0$, decrease in k_p) with increasing L_c is readily apparent. The ETC for isolated water (not shown) was highly symmetrical and was described with a large β ($\beta = 1$ for equilibrium). This suggests that the nonequilibrium exhibited by the naphthalene data in the results of a sorption-related, rather than a transport-related, process (Stromer and Kim, 1989).

To test the validity of eq 4-6, log k_p was correlated with L_c ; these results are presented in Figure 4-5. The log-linear relationship

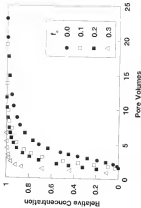


Figure 3. Relative concentration (Y-axis) vs. pore volumes (X-axis) for different values of t_p (Legend: $t_p = 0.0$ (solid circles), $t_p = 0.1$ (open squares), $t_p = 0.2$ (solid squares), $t_p = 0.3$ (open triangles)).

Table 4.1 Parameter values for negative-ion H₂O

R_0	F	B	β	α	L
0.8	0.1	4.86	0.97	0.92	24.9
0.5	0.1	2.13	0.87	0.88	23.4
0.2	0.1	0.45	0.67	1.88	20.3
0.2	0.1	1.66	0.73	0.76	9.4

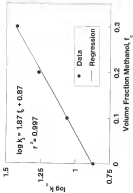


Figure 4-9 Log-20-year relationship between sorption rate constant ($\log K_s$) and fraction crystalline (ϕ_c) for high-density polyethylene in this study

predicted by eq. 4-6 appears. β is a good descriptor of the data. Equation 4-6 was further tested with the naphthalene and phenanthrene data obtained from Boyd et al. (1987). Results of expressing $\log k_2$ as k_2 are presented in Figure 5-20. Again, the log-linear relationship predicted by eq. 4-6 is evident.

The results presented above suggest that the rate of sorption of HOCs is indeed influenced by the presence of organic macromolecules and that the relationship between k_2 and f_2 is log-linear as predicted by eq. 4-6. The question then becomes, "What is the mechanistic explanation for the observed behavior?" Rate-limited intermolecular transfer across organic matter and the surface have been suggested as a primary cause for the nonequilibrium sorption of HOCs. The studies of several natural environments (Black-Glass et al., 1989; Bouchard et al., 1991) support this proposal. As discussed earlier, soil organic matter has been shown to be a complex polymeric system. The permeation of small molecules through polymers is a function of several factors including, the size, shape, and substitution pattern of the molecule and the nature and conformation of the polymer (Hogen 1991; Freeman, 1994). The conformation of a polymer is in turn influenced by the nature of the local environment, for example, a polymer will expand or contract in response to changes in solvent polarity. The permeation of small molecules is affected by this contraction/expansion. The conformation of a hydrophobic polymer will be in a relatively contracted state when near to the solid solvent. A reduction in solvent polarity as achieved by addition of an organic solvent such as methanol will result in subsequent expansion or "swelling" of the polymer. Consequently, the

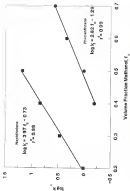


Figure 4-19. $\log_{10}$ (1/monomer concentration) versus monomer concentration (M) for naphthalene and phenanthrene data of Vond et al. (1983).

inhibition of auto-oxidation will be enhanced. A similar mechanism was proposed to be responsible for observed differences in reactivity of organic antioxidants from great interest using different solvents (Forsman and Flannery, 1941).

Considering the impact of environment on polymer conformation, it is expected that β , the constant of heterogeneous association, would also be influenced by the presence of solvent. Higher reactivity by increasing the size of the region exposed to the bulk solution, should result in an increase in the heterogeneous-association factor. Hence β would be expected to increase with increasing L_p . Inspection of Table 4-3 reveals that β did indeed increase with L_p . To further investigate the relationship between β and L_p , regression analysis were performed for two published data sets. A linear relationship between β and L_p was found for the naphthalene ($r^2 = 0.99$) and phenanthrene ($r^2 = 0.94$) data of Shieh *et al.* (1987) and for the acetone ($r^2 = 0.99$) and dioxin ($r^2 = 0.97$) data of Shieh-Glass *et al.* (1995).

Interpretation to aqueous systems

To assess the validity of extrapolating from a non-aqueous system to estimate values for k_d in aqueous systems (k_{aq}), the k_p/L_p relationship determined with only chloro-solvent data can be used to produce a k_{aq} , which can then be compared to an experimental.

Estimated k_{aq} values This was done for the naphthalene data presented in Figure 4-4. The predicted and assumed values are quite similar (see Table 4-5). This comparison was performed for the dioxin data of Shieh *et al.* (1995); the obtained k_d values for L_p values of 8.0, 8.1, 8.2, 8.3 and 8.4. The results are presented in Table 4-6. The k_{aq} values

Table 4-4. Predicted vs. measured k_{deg} values

k_{deg} (hr ⁻¹) Predicted	k_{deg} (hr ⁻¹) Measured	Δ Difference (hr ⁻¹)
3.75	3.18	5 negative
8.113	8.881	23 above
8.11	8.33	20 above

predicted from the regression eq for the alcohol-solvent data compares very well with the experimentally-determined value. This comparison was also performed for the ester data presented by Shashikumar et al.

Overall, the obtained k_{sp} values for k_p values of 0.0, 0.50, 0.7, and 0.8. Again, the predicted k_{sp} value compares very well with the measured value (see Table 4-4).

Based on the results presented above, it appears that reasonable estimation of k_{sp} values may be obtained by extrapolation from experiments performed with alcohol solvents. Furthermore, it appears that the regression equation developed in section 4-1 may be used to obtain reliable estimates of k_p values for alcohol-solvent systems.

Estimation of maximum affinity on basis of asymptote

The effect of monomer on k_p should be essentially independent of position. To test this, values of δ and α were estimated and compared with values obtained through experimentation. Recall that δ is a function of α , α and α' the slope of the $\log k_p$ - $\log R_p$ relationship. The value of α' (0.6) reported in section 4-1 was used for the latter term. A regression equation, relating α to critical/molar partition coefficient (R_{cm}), reported by Horita et al. (1961) was used to estimate values for α ; appropriate corrections were made to maintain consistency in units. Although α is a function of the alcohol/ester/solvent system (Fu and Luby, 1964a), a value of 0.15 was employed for Horita's cell (Shashikumar et al., 1961, 1967).

The parameter α is a function of the intercept and slope of the $\log k_p$ - $\log R_p$ relationship and the intercept of the $\log k_p$ - R_p relationship ($1/\alpha = \log R_{pm}$). The value of 0.301, reported in section 4-1 was used

for the $\log K_p$ - $\log K_o$ intercept. The regression equation reported by Karickhoff et al. (1979), relating the organic carbon-normalized partition coefficient (K_{ow}) to K_{ow} , was used to estimate values for K_{ow} , from which K_p values were calculated (i.e., $K_p = K_{ow}/OC$).

The predicted δ and ϵ values for the neophthalene data are 2.56 and -2.32, respectively (an experimentally-determined value of 2.266 (Karickhoff, 1980) was used for K_{ow}). These values compare relatively well with the experimentally-determined values of 1.87 and 0.87 reported in Figure 4-4. The same procedure was performed for the phenanthrene and neophthalene data of Wood et al. (1987), using an experimental K_{ow} value of 11,658 (Karickhoff, 1981) for phenanthrene. The predicted values for δ and ϵ were 3.44 and -1.48 for phenanthrene and 2.56 and -0.37 for neophthalene. Again, these values compare well with the experimentally-determined values presented in Figure 4-10. It should be stressed that the values for the parameters required to predict δ and ϵ were obtained with empirical regression equations. The ability to predict values that are close to experimentally-determined values supports the validity of eq 4-4 and also suggests that the influence of structure on sorption kinetics is quantifiable and predictable.

Deviations from Ideal Behavior

The relationship observed between K_p and K_o is dependent, in part, upon the K_p - C functionality. The sorption effects of various compounds such as n-alkanes generally follow the log-linear model, however, the effects of stronger (i.e., less polar) compounds have been observed to deviate from log-linearity (Bar and Lee, 1987). Akinori and

Yokoyama, 1987). Thus, the k_2 - d_1 functionality may be expected to include some top-downness for systems involving stronger constraints.

The slope of the k_2 - d_1 functionality, β , is dependent upon the electron-membrane surface combination specific to a given species. For example, β would be expected to increase with decreasing membrane polarity. Thus, stronger membranes would induce greater affinity, increase in resistance along stronger membranes are more prone to resistal behavior. Therefore the use of weaker membranes, such as methanol, that are more likely to follow ideal behavior is preferred.

The discussion, so far, has centered on RSCs. The influence of constraints on the rate of reaction of RSCs containing "reactive" sections is also of interest. First, that these chemicals have a greater potential to undergo specific interactions with a network. Second, they have a larger impact on the rate of reaction of these chemicals is comparable to that observed for RSCs not containing reactive functional groups. A linear relationship between k_2 and d_1 , ($r^2 = 0.82$) for a flame/flame cell system was reported by Shieh-Kline et al. (1981). To evaluate the validity of eq 4-6 for the flame data of Shieh-Kline et al. (1981), $\log k_2$ was regressed with d_1 , the resultant r^2 value of 0.70 was less than that reported for the k_2 - d_1 regression. The hypothesis was further tested with flame data reported by Good et al. (1987). Results of regression analysis showed linear functionality to be a better description of the k_2 - d_1 relationship than log-linear ($r^2 = 0.91$ vs 0.87, respectively). These results support the hypothesis that the reaction kinetics of RSCs containing reactive sections are influenced to

a linear extent by addition of molecules that are those not containing reactive substituents.

The influence of solvent on the k_p/k_t relationship for SOCs containing functional groups was further investigated by analyzing the sorption data reported by Hsieh-Hsien et al. (1985). No relationship between k_p and k_t was apparent for this data set, based on the results of regression analysis ($r^2 = 0.00$). This suggests that the mechanism creating the rate-limited sorption of aromatic was not affected by the presence of arachidyl. Interestingly, as reported above, k exhibited a linear relationship with k_t for aromatic, just as it did for the "non-polarizable" SOCs. Thus, although the instantaneous-sorption density increases with increasing k_t , the rate of sorption of aromatic is apparently independent of k_t . This behavior is in direct contrast to that observed for the "non-polarizable" SOCs. Such behavior would be expected for a substrate like aromatic, which has been shown to be prone to specific interactions with soil organic matter (Hayes, 1980; Bridges and Bolanek, 1971; Sullivan and Bolanek (1981)).

Applications

The results presented above suggest that data on sorption kinetics collected in glass columns can be extrapolated to predict the kinetics of SOC sorption from aqueous solutions. Glass columns may be utilized in bench-scale experimentation with organic substrates, especially those that are very hydrophobic ($\log K_{ow} > 3$). The use of glass columns will reduce the time required to conduct sorption experiments and may also reduce the occurrence of various artifacts, such as sorption to apparatus surfaces. Obviously, there will be some

uncertainty associated with measured values corrected by extrapolation. However, the magnitude of this uncertainty may be no greater, and in some cases may actually be less, than the uncertainty associated with values obtained from direct experimentation with very hydrophobic chemicals in aqueous systems.

The influence of cosolvents on sorption kinetics has important ramifications with respect to modeling the transport and fate of organic contaminants in the subsurface. For example, Freund (1989) has cast doubt on the validity of using the local equilibrium assumption (LEA) when modeling solute transport (e.g., Focant et al., 1990). If sorption equilibrium is attained more rapidly in systems containing a cosolvent, then confidence in LEA validity for such systems may be relaxed.

Summary

A model describing the influence of organic cosolvents on the sorption kinetics of organic chemicals was presented. This model predicts the sorption rate constant of hydrophobic organic chemicals to be a log-linear function of the fraction of cosolvent present in the system. The experimental facts presented appear to substantiate the validity of the proposed model. The mechanism responsible for this phenomenon was postulated to involve changes in conformation of the organic matter matrix, which are induced by changes in solvent polarity that result from the addition of a cosolvent. The diffusion rate (transfer of solute) within the organic matter, the apparent nature of the observed nonequilibrium sorption, is affected by changes in the conformation of the organic matter matrix. Given this mechanism, the

function of instantaneous retention (2-4), sorption would be expected to increase as the function of constant increases. This was indeed the case for the data presented herein.

Values of the regression coefficients for the relationship observed between sorption rate constants and function involved for the hydrophobic and phenanthrene data were predicted with simple empirical equations. The predicted values were reasonably close to the measured values. This provides further support to the validity of the proposed log-linear model.

The measured values for sorption rate constants in aqueous systems compared well to those predicted using regression equations developed with plant-soil data. This supports the validity of extrapolating results obtained from plant-soil systems to aqueous systems. The log-log linear inverse relationship between sorption rate constant and sorption equilibrium constant presented in section 4-1, was found to be valid for plant-soil systems. Thus, the relationship represented by eq 4-1 may be used to estimate sorption rate constants for plant-soil, as well as aqueous systems.

Deviations from log-linear behavior are expected under certain conditions. For example, the sorption kinetics of chemicals that have a greater potential to specifically interact with the solvent might be expected to be affected to a lesser extent by a molecule than are hydrophobic organic chemicals. This was shown to be the case for three data sets, the 1,1,1-trichloro-2,2,2-trifluoroethane and the polychlorinated biphenyls.

CHAPTER 3
SEDIMENT SOLUTE TRANSPORT INFLUENCED BY
MULTISCALE HETEROGENEITIES

Introduction

As discussed in the Introduction, a great deal of data has been reported that suggests that the transport of solutes can be influenced by transport-related and by sorption-related nonequilibrium processes. It is logical to assume that in some cases, especially in the field, solute transport will be controlled by both of these nonequilibrium processes. When investigating solute transport it is imperative that the potential for multiple sources of nonequilibrium be recognized and evaluated.

Nonequilibrium is often conceptually modeled using a kineticism approach, wherein the porous medium is discretized into two domains. The so-called "two-compartment", "two-region", or "two-site" mechanistical models (van Genuchten and Wieringa, 1979; Balla et al., 1979; Gossens and Klute, 1977; Kuchelshoff, 1980) that result from this approach may be used to represent all three nonequilibrium processes (i.e., structural nonequilibrium, intramolecular diffusion) (Gossens and Klute, 1977). Such models have been used extensively to simulate sorption dynamics and solute transport data. For example, van Genuchten and Wieringa (1977), Kuchelshoff and Berke (1981), Balla et al. (1981), Gossens and Klute (1977), Miller and Weber, (1981; Liu et al., 1983, Kuchelshoff et al., 1983).

A major remainder associated with hierarchical models is the assumption, implicit or explicit, that a single process is responsible for the observed non-equilibrium. As discussed above, there are likely to be situations where non-equilibrium is caused by more than one process. A model that accounts for multiple sources of non-equilibrium could be required to accurately represent such systems. For example, application of a hierarchical model to systems influenced by multiple non-equilibrium processes would yield global or lumped kinetic terms, i.e., parameters that represent the combined effects of all processes contributing to non-equilibrium. Conversely, the application of a model designed for multi-process non-equilibrium would yield kinetic kinetic terms, each representing individual non-equilibrium processes. Mathematical models are essential used to assist in the verification of the conceptual models which they represent. For mathematical models to be employed in this fashion, each of the processes of concern should be represented by a distinct term. The use of global or lumped terms, while satisfactory for purposes of estimation or fitting, is not conducive to process investigation. Hence, a model that accounts for multiple sources of non-equilibrium would be required to be of greater use in process-level investigations of system dynamics.

an obvious goal of modeling is to obtain values for all parameters independently. Such regulatory means that the necessary for collecting or fitting parameter values is designed and that independent predictions of system response to specified perturbations are possible. Global parameters are not amenable to independent determinations, because they represent multiple processes. They are, in essence,

driving parameters unique to the specific system and sets of conditions for which they were determined. Consequently, instantaneous models are not particularly useful for independent prediction of seizure response in systems influenced by multi-source competition.

The purpose of this section is to present a new model that explicitly accounts for multiple sources of desynchronization influencing seizure response in juxta neurons. The conceptual and mathematical framework of the model is described. Model parameters and their determination are discussed. A sensitivity analysis is performed to elucidate the effect and relative importance of the various parameters on seizure behavior. Finally, the model is applied to several published data sets to illustrate its use and to evaluate the validity of the desynchronization upon which it is based.

Theory

Conceptual Model

The multi-process desynchronization (MPD) model is designed to simulate seizure response in juxta nuclei where both response-related and desynchrony-related desynchronization processes contribute to the observed desynchronization. The complex dynamics of such systems are represented by a model consisting of the spatially-averaged instantaneous coupled in parallel. A schematic of the model conceptualization is shown in Figure 3-4. This conceptualization results in discrimination of the juxta system into four response domains, where instantaneous response occurs in the first domain and non-linear response occurs in the other three. In simple systems, where desynchronization may be caused by PM and

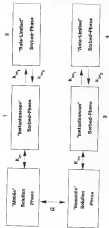


Figure 6.3. Idea space of the conceptualization space which the model used to build.

Interaggregate surface diffusion, would be an aggregated well with an aggregable organic matter confined to this system, instantaneous transfer of solute occurs between the interaggregate (or mobile) region and the surface of the organic matter situated at internal surfaces of the aggregates (sorption domain 1). Sorption domains 1 and 2 are coupled by diffusion mass transfer within the matrix of the organic matter. The mobile and the immobile (interaggregate) regions are coupled by diffusion mass transfer within the interaggregate pores (Fig. 1, 1981). Transfer between the immobile region and sorption domain 1 is instantaneous as it was between the mobile region and domain 1. The coupling between sorption domains 1 and 2 is similar to that between domains 1 and 2. Note that although mass transfer between the immobile region and domain 1 is instantaneous, reversibility of sorption "sites" in domain 2 is not hindered by mobile-immobile mass transfer. Also, note that sorption in domain 4 is controlled by two mechanisms, TDE and interaggregate surface diffusion.

The BE component in the SPE model can be used to represent any transport-related nonequilibrium process. For example, in the case of heterogeneous soil the nonequilibrium can be designated as the mobile region and the bulk soil matrix as the immobile region. The sorption-related nonequilibrium represents any reversible interaggregate surface diffusion, intramolecular diffusion or chemical nonequilibrium. For chemical nonequilibrium, the process should be one that can be viewed with a serial representation (e.g. "physiosorption" which is generally fast followed by "chemisorption", which is often very-slow).

It should be noted that an alternative conceptualization to that of Figure 3-4 could be formulated by making domain 1 and 2 is parallel to the mobile region and domain 3 and 4 is parallel to the immobile region. This model would be applicable to systems where both physicochemical and chemical-related processes cause nonequilibrium and where the chemical nonequilibrium process is best modeled with a parallel representation (e.g., sorption by two different types of sites, where sorption is rate-limited at one and instantaneous at the other). The formulation illustrated in Figure 3-4 was selected because heterogeneous water diffusion was considered to be the more predominant nonequilibrium process for HCO₃⁻ in comparison to chemical nonequilibrium.

Mathematical Model

At equilibrium, sorption in each domain is represented with the following linear equations:

$$\begin{aligned} S_{1eq} &= K_d S_{1s} C_{1s} & S_{2eq} &= F_{1s} S_{1s} C_{1s} \\ S_{3eq} &= (2-K_d) S_{3s} C_{3s} & S_{4eq} &= (1-F_{1s}) S_{3s} C_{3s} \end{aligned} \quad (3-4)$$

where S_{1s} is the mass of sorbate in domain 1 ($i = 1, 2$) attached by the mass of sorbent in the mobile region, S_{2s} is the mass of sorbate in domain 2 ($i = 3, 4$) attached by the mass of sorbent in the immobile region, C_{1s} is the solute concentration (M/L^3) in the mobile region, C_{3s} is the solute concentration (M/L^3) in the immobile region, S_{1s} is the fraction of sorbate in the mobile region for which sorption is instantaneous, F_{1s} is the fraction of sorbate in the immobile region for which sorption is instantaneous, and S_{1s} and S_{3s} are the equilibrium

capture constants (k_1^0/k_2^0) for the mobile and immobile regions respectively. The total active concentration, R_1 (mass monomers/total solvent mass) is the weighted-sum of the sorbed-phase concentrations in the two regions:

$$R_1 = f (R_{1m} + R_{1i}) + (1-f) (R_{2m} + R_{2i}) \quad (3-3)$$

where f is the mass fraction of monomer comprising the mobile region at equilibrium.

$$R_2 = f (R_3 + R_4) + (1-f) (R_{3m} + R_{3i}) \quad (3-4)$$

Recognizing that $R_{3i} = R_{3m}$ at equilibrium, eq. (3) reduces to

$$R_1 = R_3 + R_{1m} \quad R_2 = f (R_3 + R_4) + (1-f) (R_{3m}) \quad (3-5)$$

where R_3 represents the weighted-average equilibrium capture constant (k_1^0/k_2^0) for the active process system.

Isorption dynamics in both the mobile and immobile regions are described as follows:

$$\frac{dR_{1m}}{dt} = k_1 R_3 \frac{dR_1}{dt} \quad (3-6a) \quad \frac{dR_{2m}}{dt} = f k_2 R_{3m} \frac{dR_{3m}}{dt} \quad (3-6b)$$

$$\frac{dR_{1i}}{dt} = k_{1m} R_{1m} - k_{1i} R_{1i} + k_{1i} [(1-f) R_{2i} + R_3 R_{1m} - R_{1i}] \quad (3-6c)$$

$$\frac{dR_{2i}}{dt} = k_{2m} R_{2m} - k_{2i} R_{2i} + k_{2i} [(1-f) R_{1i} + R_{3m} R_{2m} - R_{2i}] \quad (3-6d)$$

where k_{1m} , k_{1i} , k_{2m} , and k_{2i} are first-order sorption kinetic coefficients ($1/t$).

The unassociated, identical re-disorption, release-kinetics equation formulated in terms of the HRR model, is written:

$$R_3 \frac{dR_1}{dt} + f_2 \frac{dR_{2i}}{dt} + f_2 \frac{dR_{2m}}{dt} + f_{2m} \frac{dR_{3m}}{dt} + (1-f_2) \frac{dR_{3m}}{dt} =$$

$$(1-f_2) \frac{dR_{1m}}{dt} - k_1 R_3 \frac{dR_1}{dt} - k_2 \frac{dR_2}{dt} \quad (3-7)$$

where δ_m and δ_{im} are the symmetric mixed moments ($\delta^2 \leq \delta_m^2$) of the mobile and immobile regions, respectively, ρ is the bulk density (g cm^{-3}) of the solid porous medium (note $\delta_m + \delta_{im} = \delta_m^2$), θ is the hydrodynamic dispersion coefficient in the mobile region (cm^2/s), q is Darcy flux (cm^3/s), and $v = q/\theta$ is average pore-water velocity (cm/s). It is assumed that adsorptive-desorptive mass transport occurs only in the mobile region. All solute mass in the immobile region is subject to mass transfer between the mobile and immobile regions:

$$v_m \frac{\partial C_m}{\partial x} + (1-\theta) \frac{\partial C_{im}}{\partial t} + (1-\theta)v \frac{\partial C_{im}}{\partial x} = \alpha (C_m - C_{im}) \quad (1-7)$$

where α is a dimensionless mass transfer coefficient ($1/\text{s}$).

Equation 1-7 may be rewritten by substituting in eqs 1-5 and 1-6

$$\begin{aligned} (1 - \theta + \theta C_m / C_m) \frac{\partial C_m}{\partial t} + \theta C_m [(1 - \theta_m) C_m / C_m - C_{im}] + \alpha (C_m - C_{im}) = \\ \theta_m \left[\frac{\partial^2 C_m}{\partial x^2} - v \frac{\partial C_m}{\partial x} \right] \end{aligned} \quad (1-8)$$

Equations 1-2 and 1-8 may be rewritten,

$$\begin{aligned} (1 + \frac{\theta_m}{\theta} \frac{C_m}{C_m}) \frac{\partial C_m}{\partial t} + \frac{\theta_m}{\theta} \frac{1}{2} [(2 - \theta_m) C_m / C_m^2 - C_{im}^2] + \alpha (C_m^2 - C_{im}^2) = \\ \frac{1}{2} \frac{\partial^2 C_m^2}{\partial x^2} - v \frac{\partial C_m^2}{\partial x} \end{aligned} \quad (1-9)$$

$$\begin{aligned} [(1 - \theta) + (1 - \theta) \frac{\theta_m}{\theta} C_m / C_m] \frac{\partial C_{im}}{\partial t} + (1 - \theta) \frac{\theta_m}{\theta} [(1 - \theta_m) C_m / C_m^2 - C_{im}^2] \\ (C_{im}^2 - C_m^2) = \alpha (C_m^2 - C_{im}^2) \end{aligned} \quad (1-10)$$

by defining the following dimensionless parameters

$$\begin{aligned} R = \frac{\theta_m}{\theta} \quad (1-11a) \quad \alpha = \frac{\alpha}{v} \quad (1-11b) \end{aligned}$$

$$F = \frac{qL}{2L} \quad (3-110)$$

$$k_a^* = \frac{k_{a0} L^2}{q} \quad (3-110)$$

$$F = \frac{k_a}{L} \quad (3-111)$$

$$k_{a0}^* = \frac{k_{a0} L^2}{q} \quad (3-111)$$

$$F = \frac{qL}{2L^2} \quad (3-112)$$

$$k_a^* = \frac{k_{a0}}{(1-F_{a0}) k_a c_a} \quad (3-112)$$

$$k_a^* = \frac{k_a}{c_a} \quad (3-113)$$

$$k_{a0}^* = \frac{k_{a0}}{(1-F_{a0}) k_a c_a} \quad (3-113)$$

$$k_{a0}^* = \frac{k_{a0}}{c_a} \quad (3-114)$$

where L is the length of interest, q is total water content ($L^3 L^{-2}$) of the entire pore medium, and k_a is input concentration. Note that the parameters described in equations 3-11 to 3-14, and 3-16, 3-17, 3-19, and 3-20, in various

Radialux models representing the three unipolarization forms included in the MPM model.

Equations 3-16 and 3-20 may be rewritten in dimensionless form as follows:

$$\frac{\partial k_a^*}{\partial \tau} = k_a^* (k_{a0}^* - k_a^*) \quad (3-21)$$

$$\frac{\partial k_{a0}^*}{\partial \tau} = k_{a0}^* (k_{a0}^* - k_{a0}^*) \quad (3-22)$$

Equations 3-17 and 3-19 may be simplified as

$$\begin{aligned} k_a \frac{\partial k_a^*}{\partial \tau} &= k_{a0} k_a^* (k_a^* - k_a^*) + k_a (k_{a0}^* - k_{a0}^*) = \\ &= k_a k_{a0}^* \frac{\partial k_a^*}{\partial \tau} = \frac{\partial k_a^*}{\partial \tau} \end{aligned} \quad (3-23)$$

$$k_{a0} \frac{\partial k_{a0}^*}{\partial \tau} = k_{a0} k_{a0}^* (k_{a0}^* - k_{a0}^*) + k_{a0} (k_a^* - k_{a0}^*) \quad (3-24)$$

by defining the following retardation factors:

$$R_{ad} = \theta + \frac{Q_d}{\gamma} V_{ad} R_{ad} \quad (3-13a)$$

$$R_{ad} = \frac{Q_d}{\gamma} (1-R_d) R_{ad} \quad (3-13b)$$

$$R_{ad} = 1 - \theta + \frac{(1-Q_d)}{\gamma} V_{ad} R_{ad} \quad (3-13c)$$

$$R_{ad} = \frac{(1-Q_d)}{\gamma} (1-R_d) R_{ad} \quad (3-13d)$$

From eqs. (3-6) and (3-13), note that the total retardation factor, R , is given by

$$R = R_{ad} + R_{ad} + R_{ad} + R_{ad} = [1 + (\gamma/Q) R_d] \quad (3-14)$$

Relative or fractional retardation parameters may be defined as follows:

$$\beta_1 = \frac{R_{ad}}{R} \quad (3-14a) \quad \beta_2 = \frac{R_{ad}}{R} \quad (3-14b)$$

$$\beta_3 = \frac{R_{ad}}{R} \quad (3-14c) \quad \beta_4 = \frac{R_{ad}}{R} \quad (3-14d)$$

Note that the four β values sum to unity and that β_4 represents the fraction of retardation that is introduced by sorption in domain 1.

It is apparent from eqs. 3-2a, 3-2b, and 3-2 that the electrostatic term (domain approximation) is employed to represent both the physical nonequilibrium and sorption nonequilibrium processes. Such an approach is based on the linear driving-force approximation, first presented by Glasstone¹ and further refined by (1947). An alternative representation for FBE could be obtained with the use of diffusion equations based on Fick's law. A great deal of work utilizing the diffusion-based approach has been reported in the chemical-engineering literature. Such an approach

was used by Rao and coworkers to describe solute transport in aggregated media (Rao et al., 1976a,b; Shukla-Rao et al., 1980) and more recently by several others (e.g., Gifford et al., 1981; Metcalfe et al., 1981; Roberts et al., 1987; Miller and Baker, 1988). Use of the diffusion-based approach requires detailed knowledge of the physical structure of the porous medium and is complicated by several factors, including complex structural shapes, size-distributions of the structures, and the presence of poorly-defined structures. These and other factors restrict the number of cases to which diffusion-based models can be satisfactorily applied. For this reason, the mass-transfer approximations are used. Several investigators have shown that models utilizing the mass transfer approximations provide simulations similar to those obtained from diffusion-based models (e.g., Rao et al., 1976b; Hughes and Redden, 1980; van Gesselom, 1981; Parker and Valocchi, 1982).

A computer program developed by Jeng (1986) was used to solve the pertinent governing equations (3-11 to 3-15) under the following initial and boundary conditions:

$$C_{0i}^T(x,0) = C_{0m}^T(x,0) = 0 \quad (3-16a)$$

$$C_{0i}^T(x,0) = C_{0m}^T(x,0) = 0 \quad (3-16b)$$

$$C_{0i}^T = C_{0m}^T = \frac{1}{2} \frac{R_0^2}{\pi^2} \frac{\partial^2 C_{0i}^T}{\partial x^2} \quad (3-16c)$$

where

$$C_{0i}^T = 1 \quad 0 \leq x \leq x_0 \quad (3-16d)$$

$$C_{0m}^T = 0 \quad x \geq x_0$$

and $\Gamma_0 = \text{pulse width}$

$$\frac{\partial^2 \phi_{\text{ex}}}{\partial \xi^2} \bigg|_{\xi=0} = 0, \quad \xi > 0 \quad (14b)$$

Performance of the numerical solution was checked against an analytical solution (Huang, 1987) for several simplified cases (Huang, 1988).

The computer program developed by Huang (1988) was based on the finite-difference method and utilized the Crank-Nicolson technique with equal weighting for the time component of the diffusion equation. The central difference technique was used for the space component of the equation. The discretization (i.e., number of grids) for the spatial component was optimized based on the value of the Fourier number; the number of grids ranged from 20 to 40. The discretization for the temporal component (Δt , time interval) was optimized based on the values of several parameters of the governing equations (Huang, 1988).

From eq. 3-15b, it is apparent that a flux-type boundary condition is being employed. It has been widely discussed in the literature, this type of boundary condition is more appropriate than a concentration-type condition for miscible displacement experiments (e.g., van den Hulst and Jansen, 1980). It is unusual for this article's formulation that sample effluent represents interfacial solution, or in other words, represents flow-weighted concentrations. The boundary condition beyond eq. 3-15b is then employed by Huang (1987) and allows the determination of flow-weighted concentrations at $\xi = 1$. It has been shown that calculations produced with a solution employing this boundary condition are similar to those produced with a solution employing the assumption of a semi-infinite column with no boundary effects occurring

to the authors, the P parameter does approximately 1 (see Grossmann and Berlin, 1980).

Parameter Determination

Determining the values for a model's input parameters often proves to be the most difficult task in modeling. One method used routinely in the curve-fitting of model simulations to experimental data, wherein the parameter values are determined by optimization. The KPM model was coupled to a nonlinear, least-squares, optimization program (Gauss, Savier and Wells, 1988) to allow parameter determination in this fashion. A model's conceptual basis is truly tested and validated only when the model can simulate a set of experimental data with all parameter values determined independently of the data being simulated. A general scheme for obtaining the parameter values required for the KPM model, is presented below.

Initial number, N

P represents the contribution of hydrodynamic dispersion to solute transport. Hydrodynamic dispersion is generally considered to be comprised of two components: molecular diffusion and mechanical dispersion. The contribution of diffusion to hydrodynamic dispersion is generally insignificant, especially in the range of velocities typical to many cases of interest. As a result, all solute transport essentially the rate dispersive transport. The P value determined from the breakthrough curve of a nonreacting solute may therefore be used for reacting solutes. In using the KPM model, it is assumed that N is known. Under such conditions, the EC of a nonreacting solute will

exhibits nonlinearity (e.g., asymmetry, hysteresis) (Quasthoff and Reij,

1993). A bifurcation model should be used to simulate the RFE in such cases.

Relaxation Factor (β)

There has been much discussion in the literature on the validity of using K_p values determined from batch sorption experiments in calculating β values for use in modeling column experiments. If conditions for the batch experiments are constrained to be as similar as possible to those of the column system, and if various corrections are attempted, β values calculated from sorption isotherms may be successfully used for column systems (e.g., van Duizend et al., 1977; Meek-Clune et al., 1981, 1989; Lee et al., 1988). Other means of determining β values include (1) measuring the area above the RFE for a frontal input (e.g., Roberts et al., 1980; van Duizend and Verier, 1984; Meek-Clune et al., 1987); (2) determining the first temporal moment for a pulse input (e.g., Roberts, 1980; Salaschi, 1985); and (3) the use of various correlation equations relating K_p to properties of the sorbent and the solute (e.g., Olson et al., 1979; Lyman, 1982; Karickhoff, 1983).

Relaxation factor representing TDE (β_d)

TDE primarily represents the contribution of TDE to total nonequilibrium. When TDE is present, the RFE of a sorbing solute will exhibit nonlinearity and should be simulated with a two-region (2 + two-region) model, as mentioned above. Values for w and β are determined by fitting the two-region model to the RFE of a sorbing solute. When TDE is a partitioning process, the w value determined for a sorbing solute may be used for a sorbing solute as well. The w

value must, however, be corrected for differences in the diffusivities of the two solutes.

The first-order mass-transfer coefficient (a) for the PBL term can be related to the diffusion coefficient using an equation of the following form (Hirawan and Lee, 1987 and references cited therein):

$$a = \frac{u D_p}{r^2 l^2} \quad (3-10)$$

where D_p is the diffusion coefficient in water (m^2/s); r is a correction factor, u is a geometric shape factor, and l is the characteristic diffusion length. For pore diffusion, the latter three terms are characteristics of the porous medium. Hence, for a given porous medium, the only solute-specific term in eq. 3-10 is D_p . The a value for a sorbing solute (and for other nonreacting solutes) can therefore be determined from that of a nonreacting solute by use of the following equation:

$$a = \frac{a_{ns} \gamma \lambda}{\eta} \quad (3-11)$$

where a_{ns} is the first-order mass-transfer coefficient calculated from the a value determined for the nonreacting solute and where

$$\eta = D_p/D_{ns} \quad (3-12)$$

is not a representing the diffusion coefficients for the sorbing and nonreacting solutes, respectively. Note that the corrected value of a for a sorbing solute will usually be smaller than the a value for a nonreacting solute, since $D_p < D_{ns}$ and $\gamma < 1$. i.e., the diffusion coefficients for sorbing solutes are generally smaller than those of solutes employed as tracers in a simulated water plume(s).

Isobutyl acetate homopolymer, IPI, (2)

k_p^* and k_{tr}^* represent the contribution of isobutyl homopolymerization (IPI) to the total homopolymer influencing chain transport.

Independent determination of isobutyl kinetic parameter values has received little attention in data. One approach for obtaining such values is an independent experiment for isobutyl initiation, such as the batch-test or the gas-phase descriptive methods.

Another approach would be the use of an empirical correlation equation that relates the isobutyl-rate coefficients to the equilibrium isobutyl coefficients, as presented in section 4-1. The regression equation reported in Figure 4-2 for the Type-I data may be used to estimate isobutyl kinetic coefficients (k_p) for IPIs. These values then may be used in conjunction with eqs. 3-11b and 3-11c to estimate values for k^* . The same approach may be attempted for IPIIs, using the regression equation reported for the Type-II data. However, the k_p values estimated for IPIIs will have greater uncertainty because, as discussed above, IPIIs are more likely exhibit a series of IPIIs rather than a single one.

It should be noted that the definition of k^* as given in eqs. 3-22b and 3-11c is not equivalent to the definition used for the equivalent Isobutyl number in the reaction model, which is $k_p^*k_p/(k_p + k_{tr})$ (cf. van den Hulst, 1961; see, e.g., cf. 1981). The definition of k^* can be modified in the following manner:

$$k^* = k_p^*/(k_p + k_{tr}) \quad (4-17)$$

be infinite reproducibility with that of the concrete model. This modification will be needed when comparisons are made between the SPH model and the bioclimatic models.

Validation of Functional Description Parameters (FDP)

Four terms representing the contribution of each of the four major functions to total photosynthesis, are the most difficult to determine independently. P_0 represents the fraction of instantaneous photosynthesis ($P =$ crop yield). For an aggregated cell, the amount of nitrogen absorbed at some small time interval in a batch experiment could be used to estimate P_0 . To independently determine values for all four P terms, knowledge of P_{max} , P_{min} , and f is required. Values for the P 's could be determined by fitting a bioclimatic model to the results obtained from a kinetic experiment. Values for f may, in certain cases, be determined either experimentally or by direct measurement of physical properties of the protein medium.

Modeling Analysis

The SPH model introduces considerable complexity into the scaling transport equation. In comparison to that imposed by the models employing the bioclimatic compartmentalization assumption and especially the local equilibrium assumption (LEQ). It is important to identify the conditions under which the use of the SPH model is warranted and the conditions for which the bioclimatic model is adequate. This endeavor is, in nature, one of identifying the conditions under which the LEQ is valid. Consider, for example, a case where compartmentalization is caused by a transport-related and a reaction-

related process. When recent conditions are such that the LRA is valid for one of the two interpollution processes, the RPD model reduces to the instantaneous model. Therefore, if the LRA is valid for both processes, a LRA-based model would be appropriate.

Identification of the conditions under which the LRA is valid has generally become a focus of attention. A component of this research has been the development of criteria that may be used for evaluating LRA validity. The Bushblom number has been the most widely used criterion, which is not surprising given that the Bushblom number is a ratio of hydraulic residence time to reaction time and, as such, characterizes the degree of interpollution. The use of Bushblom numbers as LRA-validity criteria has been discussed by many others, Bologh et al. (1982), Rao and Jangay (1983), Jennings and Rikman (1984), Tolosa (1985), and Suter and Smith (1987). The use of Bushblom numbers as LRA-validity criteria has been criticized by Tolosa (1987) on the basis that parameters other than Bushblom numbers can influence LRA validity.

To quantitatively evaluate LRA validity one must have, in addition to a criterion, a means to measure deviations from 'ideal' behavior (i.e., that exhibited under conditions where LRA is valid). A method based on comparison of time moments of the relative RPD was presented by Tolosa (1988) and Smith and Tolosa (1988). A quantitative error criterion was defined as

$$E_e = (V^2_{\text{e}} - V^2_{\text{LRA}})/V^2_{\text{e}} \quad (2-24)$$

where V_e is the sixth central time moment and the superscripts E and L refer to the interpollution and LRA models, respectively. Expression of

eq 3-15 shows that k_p will increase as departure from conditions of local equilibrium increases and that $k_p = 1$ when this is valid.

The degree of "spreading" or dispersion is often used to characterize chemical volume transport. The second central temporal moment formula for the LRE model for a square, finite pulse, was given by Fisher and Tolosa (1981)

$$k_p = (D^2/P) + (D^2/p)(1) \quad (3-16)$$

In eq 3-16, the dispersion influencing volume transport is seen to be comprised of two components, hydrodynamic dispersion and that related to a finite input pulse. The equation for the second central temporal moment for the RFE model may be written in a manner similar to that employed by Tolosa (1982) for the bimolecular model:

$$k_p = (D^2/P) + (D^2/p^2)\beta + (D^2/p^2)\beta_0 + (D^2/p^2)\beta_{\infty} + (D^2/p)(1) \quad (3-17)$$

Inspection of eq 3-17 shows that each of the three nonequilibrium terms in the RFE model, along with those related to hydrodynamic dispersion and finite pulse, contribute to observed dispersion. This linear additivity, where total dispersion is the sum of the contributions of each dispersion-causing component, has long been recognized in chromatography (e.g., Gliddings, 1961).

The quantitative wave criterion for the RFE model is

$$k_p = P(\beta^2/\beta_0 + \beta^2/\beta_{\infty} + \beta^2/\beta_{\infty}^2) \quad (3-18)$$

when the influence of k_p is neglected. Inspection of eq 3-17 shows that LRE validity, as measured by k_p , is a function of P , the β 's representing the three rate-limited sorption domains, and the three desorption numbers. This concurs with the analysis presented by Tolosa (1982) and Fisher and Tolosa (1981). Note that the relationship

factor B does not appear in eq 3-27. LK validity is, therefore, not explicitly influenced by B . Although B does enter into eq 3-27 through the β term (see eq 3.1), in the case the value of B itself that is important, but rather the ratio of B_0 (distortion associated with eqn 1) to B , which is represented by β_0 .

The influence of metal parameters on the validity of the LK can be assessed with eq 3-27. As evident from eq 3-27 and as discussed by Tolmoch (1980), the magnitude of deviation from LK is directly proportional to P . This intuitively is a function of the manner in which the error criterion is defined. The criterion represented in eq 3-27 is an absolute measure. It can be shown that LK validity is, in fact, independent of P if a relative approach is employed. Consider, for example, a case where $P = 10$, $\omega = 1$, $\beta_0 = 0.15$, and $K'_a = K'_{a0} = 10$; the associated B_0 value calculated with eq 3-27 is 0.475. This value may be compared to that obtained for the case where the bimolecular model is valid ($\omega = 1$, K'_a tends to infinity); that value is 0.405. As expected, B_0 is larger for the case where the additional, surface-related parameter contributes to rate-equilibrium. The deviation between the two B_0 values is 18%. Now consider two additional cases where all parameter values are identical to the previous two cases except for the value of P , which is now set equal to 100. The resulting B_0 values are 0.71 and 0.43 for the cases $K'_a = 10$ and K'_a tending to infinity, respectively. The magnitude of the B_0 values for $P = 100$ are greater than those obtained for $P = 10$. However, the error between the two larger values is 40%, the same as that between the two smaller values. Hence, it is seen that in a relative sense the validity of the LK is

not a function of β . This fact was also demonstrated by Savitsky and Kolman (1984).

The two sets of parameters influencing relative LR sensitivity for the MSE model are the β 's representing the three nonpollution sources and the three baseline values associated with these sources. A typical range of values for the three β 's is 0.1 to 0.5. The baseline values may be expected to range from 0.01 to 100, which is much greater than the range reported for the β 's. It is logical to concentrate on the parameter that has the greatest potential for variation than preliminary sensitivity analysis. Hence, in the sensitivity analysis presented below, attention will be focused on the baseline values.

A sensitivity analysis of the MSE model for W^2 is presented in Figures 3-6. Note that, for this discussion, it is assumed that $W_{\text{air}} = W_{\text{soil}} = W_{\text{water}}$, and that W^2 is used to indicate equivalency with the bioassay model (see eq. 5-11 and relevant discussion). When W^2 is greater than 10, the MSE statistics converge to that of the bioassay model, becoming essentially identical at a value of 100. The contribution of organic nonpollution to total nonpollution is relatively insignificant under conditions where W^2 is greater than 10, and becomes virtually constant at values approaching 100. A bioassay model representing only the influence of MSE could be adequate in these situations. The W^2 value at which organic nonpollution becomes relatively insignificant is a function of the relative sizes of the organic sources (α 's), the β values, however, this functionally exhibits low sensitivity. Of course, if $\beta_1 = \beta_2 = 0$,

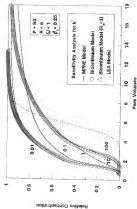


Figure 5.2 Sensitivity analysis of MVR model for k'

the model becomes totally insensitive to k_1^2 . We note, however, connected with cases where $\beta_1 = \beta_2 = 0$ (1.2.1), where the SPH model is applicable)

When $k_1^2 = 0$ (1), the SPH simulation is similar to a two-stream simulation wherein the value for k_1 is defined by one-half. For $k_1^2 \neq 0$ (1), the rate of wave transfer is so slow that the complex non-equilibrium response has minimal effect on stable transport.

For case studies 1 and 2 see, in summary, collected off and domain 1 and 2 thus become the primary active regions of the present section. As a result, apparent stabilization of the state is induced by $\beta_1 + \beta_2$.

A sensitivity analysis was performed for the case where k_1^2 is not equal to k_{th}^2 . Because k_{th}^2 is the source for a bi-modal system of mechanisms (see Figure 1-1), its influence on stable transport is expected to be dependent, in part, upon the value of w . From the results of the sensitivity analysis it appears that for w equal to some value T the SPH model is insensitive to k_{th}^2 . For values of k_{th}^2 greater than T and unstable for values less than T . This functionality holds for conditions where w is greater than some threshold or critical value, w_c . When w is less than w_c , the model is completely insensitive to k_{th}^2 . The value of w_c is a function of the size of domain 1 (1.2.1), an approximate range for w_c appears to be 0.1 to 0.25. It may be concluded that, for cases where the system is relatively insensitive to k_{th}^2 , setting k_{th}^2 equal to k_1^2 should not adversely affect performance of the model. Hence under these conditions the values of parameters for which independent knowledge is required is reduced by one.

A sensitivity analysis for w is presented in Figure 1-3. Similarly to complex non-equilibrium, the lowest relatively insignificant of w

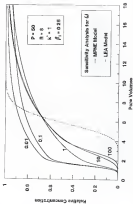


Figure 2-3 Sensitivity analysis of MPPM model for Q

values greater than 10. As the value of α tends toward 100, the RPE simulation converges to that of a binomial model representing only the contribution of active participation (not shown). As was the case for k^2 , the α value at which RPE becomes relatively insignificant is only slightly sensitive to β . At the lower limiting value of $\alpha = 0.01$, the behavior is again similar to that observed for RPE. In this case, however, the rate of rate increase between the active and inactive regions is so slow that domains 1 and 4 are effectively switched off leaving 1 and 2 as the predominant active domains.

Close scrutiny of Figures 3-2 and 3-3 shows some differences between the two cases. For values of α less than approximately 10, deviations exist between the simulations where α was fixed at 1 and k^2 was varied (case 1, Figure 3-2) and where k^2 was fixed at 1 and α was varied (case 2, Figure 3-3). The degree of divergence is observed to increase as α decreases. These deviations result from differences in the status of the inactive part when for the two cases. The degree of interaction between the inactive and active part when regions is not influenced by k^2 whereas it is influenced by α . For example, for case 1 when k^2 equals 0.01, the inactive part when remains in active participation. However, for case 2 when α equals 0.01, the inactive part when is restricted from significant participation.

The RPE of a remaining value is often used to assess the existence and relative importance of RPE. This approach may result in erroneous conclusions. Consider for example a case where an α value of 10 was obtained by fitting a binomial model to a RPE for isolated water. Based on this value, one might conclude that the contribution of

PRE was relatively insensitive for all values. However, if $\gamma = 0.25$ (see eq. 3-12) for a particular working volume, the w value for that volume would be 2.5. The conclusion that PRE is insignificant may not be valid for this volume. As discussed above, the w value obtained from fitting a homogeneous model to the RPD of a remanaging volume (v_{RM}) applies here for a working volume after correcting for differences in elasticities. Hence, $w_{RM}\gamma$ and not w_{RM} should be used as the value with which to evaluate the relative significance of PRE for working volumes.

The four limiting cases for the RPD model with respect to the nonequilibrium parameters (α , ... threshold constant) are given in Table 3-1. Note that cases 1 and 2 are equivalent when $R_1 = R_2$. Simulations produced by the RPD model for the limiting cases are compared in Figures 3-4 to simulations produced by a model employing the LRA. Note that values of 100 and 0.01 were used in place of α and R_1 , respectively. The simulations produced by the RPD model closely match those of the LRA model for all four cases. For example, the simulation produced by the RPD model when $\alpha = R^2 = 100$ is essentially equivalent to the simulation produced by the LRA model with $R_1 = 4$. In other words, the RPD model reduces to the LRA model when $\alpha = R^2 = 100$.

The equivalency between the RPD and LRA models shown in Figures 3-4, in addition to the analyses presented in Figures 3-1 and 3-3, suggests that the values of 100 and 0.01 are close approximations of the true limiting-case values of α and R_1 , respectively. These values, then, may be considered as the upper and lower bounds to the domain of significance for nonequilibrium.

Table B-3 Limiting cases

Case Equivalent	RRR Model	LRM Model
1	$\frac{\sigma}{k^2} = \frac{\sigma}{k^2} = \frac{\sigma}{k^2}$	$R_2 = 1$
2	$\frac{\sigma}{k^2} = \frac{\sigma}{k^2} = \frac{\sigma}{k^2}$	$R_2 = 1 (R_1 + R_2)$
3	$\frac{\sigma}{k^2} = \frac{\sigma}{k^2} = \frac{\sigma}{k^2}$	$R_2 = 1 (R_1 + R_2)$
4	$\frac{\sigma}{k^2} = \frac{\sigma}{k^2} = \frac{\sigma}{k^2}$	$R_2 = 1 (R_1)$

Note that cases 2 and 3 are equivalent when $R_1 = R_2$.

R_2 is the equivalent correlation factor for the LRM model.

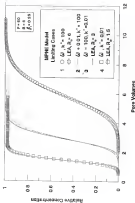


Figure 3.4. Clustering curves for the MHM model

The purpose of Figures 3-1 and 3-2 and of Figure 3-4 was to appraise the conditions under which the SPSS model conforms to the Macrominor model and the LM model, respectively. The magnitude of the Bonferroni number was used as the criterion for this appraisal. As mentioned above, the Bonferroni number has been used by others as an LM-validity criterion. Results of their analyses showed the limiting Bonferroni number value for LM validity to be approximately 100 (Osloph et al., 1970; Jennings and Kirkner, 1984; Valocchi, 1985; Jahn and Rubin, 1987; Isenay, 1984). These numbers are in agreement with those observed herein. Jennings and Kirkner (1984) reported a Bonferroni number of 18 as being sufficient to produce a 'reasonably good approximation' of LM. This value is also in accord with the results presented above.

It should be noted that, while the sensitivity analyses presented above were performed for one value of F and R , the conclusions drawn from the analysis are applicable in a relative sense, to any F and R values, based on the discussion presented at the beginning of this section.

An important point regarding apparent retardation factors is illustrated in Figure 3-4. For limiting cases 1, 2, and 4, the vertical portion of the EPRs of the SPSS model are essentially coincident with those of the LM model. The SPSS model EPRs, however, exhibit tailing, whereas the LM model EPRs do not. The magnitude of this tailing is great, considering that the areas above the SPSS-model EPRs was the same for all simulations including case 1. The above proximity of the tail to $F^* = 1$ may, in some cases, preclude recognition of its existence

Retardation Factors are generally independent in these cases and attempts to determine such values result in apparent retardation factors that are lower than the true value. These apparent retardation factors often exhibit a velocity dependence, which confounds efforts to analyze sorption dynamics. The use of apparent retardation factors thus may lead to various problems, especially when the nature of these apparent values is not recognized. To achieve resolution in cases such as these, alternative experimental techniques are required. One such technique, called flow interruption, was presented in section 3-4. It should be noted that the use of apparent retardation factors may be adequate for some purposes, for example, estimating the overall time of peak concentration.

The effect of nonequilibrium on solute transport is illustrated in Figures 3-2, 3-3, and 3-4. In general, a BTC is rotated clockwise and is shifted leftward under conditions of nonequilibrium, thus becoming asymmetrical and skewed. When neither nonequilibrium process is important, the BTC is equivalent to that obtained with the likelihood model (limiting case II). As one process becomes increasingly significant (while the other remains insignificant) the BTC is displaced leftward as predicted by a likelihood model. In the second nonequilibrium process case two effect, the BTC is displaced further leftward toward limiting case 4. This additional displacement cannot be explained by a likelihood model.

Model Evaluation

To illustrate the use of the MPM model and to evaluate the validity of the model's conceptual basis, the model was applied to several published data sets. All of the systems from which the data were obtained are aggregated cells with nonlinear organic nuclear kinetics. All of the experiments were performed in pulsed columns under conditions of steady inlet flow using slablike displacement techniques. Several approaches were used to obtain independent values for the model parameters. In some cases, the approach employed may not represent the most desirable, however, the most desirable is often not possible given the constraints of limited data. In these cases, the least-alternative approach is selected. It is hoped that the examples discussed below will serve as a useful illustration of the various strategies available for parameter determination.

Example 1

The first group of data sets in which the MPM model was applied is that of van Gemmen et al. (1977). They presented PDCs obtained from slablike displacement of the fissionable ^{235}U through columns pulsed with an aggregated cell (Ottensmeyer loss, organic matter content = 2.5%). The purpose of these experiments was to evaluate the performance of a two-region model developed by van Gemmen and Kiersting (1976). The conclusions resulting from a three-parameter (β , β_0) optimization of the data compared well with the experimental PDCs, although not as well as did the optimized simulation of a one-region scheme (Ottensmeyer, 1978). Reported in a companion paper (Van Gemmen and Kiersting, 1977)

However, the Péclet numbers determined from the 2.4 kV data were smaller than those obtained from the voltammetry data. Hence the Péclet number determined for trichloro water should also hold for 2,4,6- Cl_3 -T, the presence of an additional nonequilibrium process is suggested. This was noted by van den Hulst et al. (1971) and was accounted for in their kinetic model.

The first data set obtained for van van Dine Experiment 1-b ($v = 8.45$ cm/hr, aggregate diameter is 2 cm). The performance of the homogeneous and HPM models will be tested by comparing independent predictions of the experimental RDC. For the homogeneous model, the Péclet number was obtained from optimization of the corresponding trichloro-water RDC with the homogeneous model. The B value was calculated with the linearized B_p value obtained by van den Hulst et al. (1971) from a batch leaching experiment, in which it was determined that sorption was nonlinear ($n = 0.78$, where n is the Freundlich exponent). For this case, it is assumed that DB is the only source of nonequilibrium. Hence, the α value obtained from optimization of the corresponding trichloro water RDC with the homogeneous model is used, after correcting for differences in diffusion coefficients. The Rayleigh and Smith (1974) equation was used to calculate diffusion coefficients, which were then used to calculate $\alpha = 0.5$ using eq. 5-12. β then, is the only remaining parameter to be determined. A simplifying assumption of $\beta = 4$ (Onda-Rios et al., 1986) was made in order to estimate a value for β . This assumption is based on the idea that the flux/mass-transfer between water and gas-phase paracetamol domains $\{q\}$, as determined from fitting the homogeneous model to the RDC of a nonaching

which is equivalent to the Fermi-Dirac function while and inside the crystal domain [1]. Although this assumption is not expected to be generally valid, it serves as a useful first approximation. The value for β obtained from application of the crystalline-field EFC to 3.15, the β value estimated by assuming $d = 0.75$ to 0.81, shows $\beta = (q + 7.0d)/5$ (see Gendron et al. [17]).

With the procedure used above, values for all model parameters have been determined from independent sources. When such is the case, the model may be used in a predictive mode. The independent prediction produced by the Monoclinic model is presented in Figure 3-3. The experimental EPR exhibits a significant induced shift ($\delta = 1$, early breakthrough) and an asymmetrical profile in comparison to the model prediction. The early breakthrough and asymmetry exhibited by the data suggests the presence of an additional noncollinear mechanism. If such an additional mechanism were present, the EPR model should provide an improved simulation of the data. The values for P , Q , and ω were obtained for the EPR model in the same manner as described for the Monoclinic model. To reduce the number of independent parameters, it was assumed that $K'_{\text{II}} = K'_{\text{III}} = K'$ an assumption that would seem reasonably valid for the species involved. If the additional noncollinear mechanism involves site-distorted interactions between the solute and the solvent ligands nearest, the regression equation presented in Figure 4-1 may be used to estimate a value for b_2 . The equation for the Type-II character can used, given the character nature of 3.4 3-7. Equation 3-13a may then used to calculate a value for K'

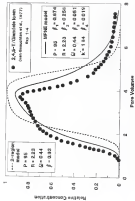


Figure 3.3 Independent partitioning of data of van Simons et al. (1977) produced with the 4-region and the 3-region models.

The remaining unknown parameters are β_1 , β_2 , and β_3 . It will, thus, be found that the best fit is not unique. Equations 2-28 and 2-29 may be used to calculate values for these parameters if P , β , and d are known. Employing the same assumption that $\beta = d$ as used above, β is the remaining unknown parameter. A value of β is used to account for P based on the work of Barikbaff (1986) and Barikbaff and Morris (1987) who evaluated empirical kinetics for several SBR/well systems with a biocontinuous model.

The independent prediction produced by the RSM model is presented in Figure 3-5. Comparison of this prediction with that of the biocontinuous model shows that the RSM model provides a much-improved description of the data. This supports the assertion that more than one nonequilibrium process is affecting the transport of H_2S (4). The success of the RSM model in predicting the data suggests that the conceptual model upon which it is based is sound.

A multi-parameter (β_1 , β_2 , β_3 , α , K^*) optimization of the data was performed with the RSM model. The optimized values for α and K^* were 0.44 and 0.1, respectively. The value of the optimized α is the same as that calculated with the α for isolated meter, after employing eq. 2-1 as a correction for differences in substrate rates. The equivalence of the calculated and optimized α values supports the validity of obtaining an α value for a reacting solute from the RM of a nonreacting solute.

The k_2 value determined from the optimized K^* is approximately a factor-of-three larger than the k_2 value calculated from the k_2 vs β_2 regression equation. A difference that is within the scatter of the data used to develop the equation. Although this discrepancy may be

Development, it may also support the suggestion that the sorption-related process involved in this system is comprised of a rate-limited interaction between 2,4,6-T and various organic matter. The sorption of 2,4,6-T to diatoms will be perturbed by organic matter (Pflüger and Andersen, 1994). If sorption is controlled by organic matter, it is probable that the sorption-kinetics mechanism would involve organic matter as well. Such a mechanism was suggested as the cause for the nonequilibrium sorption exhibited by 1,4-B (Pflüger, 1993; Section 5-2), a chemical of similar usage.

Model simplification is often carried by using the parameters obtained from optimization of one set of data to predict another set of data. Data from experiment 1-3 of van Duin et al. (1977) ($\nu = 1.5$ cm/hr, aggregate diameter 4.1 m) were used for this purpose. Values for P , B , and α were independently obtained in the same manner as described for the independent predictions of experiment 1-4. With K'_a and K'_{im} set equal to K' , four parameters require optimization (B_1 , B_2 , B_3 , K'). The 4-parameter optimized simulation of experiment 1-3 is presented in Figure 5-3. The b_2 value calculated from K' is similar to the b_2 value calculated from the optimized K' value obtained from experiment 1-4 (114 minutes). The closeness of these two values to that predicted with the b_2 or B_2 regression equation is again suggestive of rate-limited sorption-organic matter interaction as the nonequilibrium mechanism.

The parameters determined for experiment 2-3 were used to predict the BQ obtained from a different column experiment performed using similar conditions (experiment 1-2, $\nu = 1$ m cm/hr, aggregate diameter 2.1 m). Note that all parameters except for P and B were obtained from

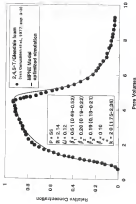


Figure 3.4 Two-parameter optimized simulation of data of van Goulet et al. (1973) plotted with the same axes. The conditions normally for optimized parameters are listed in parentheses

experiment 3-3. The values for α and β were adjusted to account for the slight differences in velocities between the two experiments. If and β were obtained from the fit of the biexponential model to the vitrified water DSC and the total isopropyl isobutene, respectively. Thus, all parameter values were obtained from independent sources. The resultant independent prediction is presented in Figure 3-3b. The parameters determined for experiment 3-3 were also used to predict the DSC of experiment 1a (see Figure 3-3b), a system with a velocity and an aggregate size unrelated than of experiment 3-3. Note that, again, all parameters were obtained independently and that the values for α and β reflect adjustment for differences in velocities. Thus the same values for the nonequilibrium parameters (α , β , β_0 , β_1) can be used to predict two experiments with different velocities and aggregate sizes, suggesting that the nonequilibrium processes are relatively insensitive to changes in velocity and aggregate size, at least over the range of values associated with these two experiments. While β_0 would be expected to be independent of aggregate size, α would be expected to be dependent (see eq. 3-30). The additional insensitivity would thus suggest that a reaction-related (α , β_0 -controlled) process is involved.

Table 3-1

The second data set to which the DSC model is applied is that of Brinsky (1979). He investigated the influence of aggregate size on kinetic displacement of the hydroxide dissociation through various packed with large time (average initial content = 1.7%) aggregates of

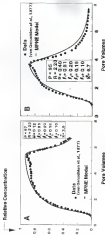


Figure 3-2 Independent prediction of data of van Krevelen et al. (1972) with strong model. (A) exp. A.1, (B) exp. 1.4.

these size ranges were prepared by treating the soil with a dilute solution of $\text{Ba}(\text{OH})_2$, a soil conditioner. RFEs obtained for chloride, employed as a leaching tracer, are shown in Figures 3-5. The RFE for the column packed with the largest aggregate (1-2 mm diameter) exhibits behavior consistent with that of a PDE-influenced system. Conversely, the RFE for the column packed with the smallest aggregate (35-65 μ m diameter) is apparently not influenced by PDE, given the large Peclet number obtained from the fit of the Bromberg solution. If PDE is not present, the Haverkamp model may be used to describe the flow-through RFE obtained for the small-aggregate column.

A two-parameter (2P) optimized simulation of this RFE is presented in Figure 3-6. The nonlinear, least-squares, optimization program NITN (van Duin et al., 1980) was used to determine the two unknowns. The value for P was determined from the chloride data and R was determined by curve analysis, i.e., using the first, normalized, chloride temporal moment. The nonoptimization exhibited by the small-aggregate data would seem to imply that a sorption-related process, given that the nonoptimal chloride data exhibited no nonoptimization behavior for P and R , were determined from the P and R values. If PDE is present in the large-aggregate/chloride system and if PDE is present for the small-aggregate/fertilizer system, it is logical to assume that the Haverkamp RFE for the large-aggregate column is influenced by both transport- and sorption-related nonoptimization. Hence, the need for the 3PFE model.

Parameter values for the 3PFE model were obtained in the following manner. The Peclet number was obtained by fitting a Haverkamp model

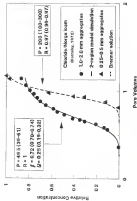


Figure 1.8 Analysis of chloride data of Bromley (1970).

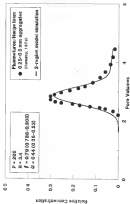


Figure 2-4 3D percolation (left) simulated simulation of loosely, (100) flomation data (small aggregate volume) with simulation model

of the chloride ME obtained from the large-aggregate column. The α value was also obtained from the same chloride data; the correction factor (eq. 3-12) was calculated and applied in the same manner as discussed previously. The value for the retardation factor (R) was determined by mixed analysis. A value for k' was calculated (eq. 3-11a) using the k_1 value determined from the diameters/small-aggregate column data. Values for the first P terms were calculated with eqs. 3-13 and 3-14. A value for P was obtained from the diameters/small-aggregate column data. A value for q was determined from the SEC of the chloride/large-aggregate data. Except for f , all other parameters in eq. 3-14 are known. The simplifying assumption of $f = q$ was used as above.

Values for all of the parameters of the RPEL model have now been determined independently. The independent prediction of the diameters ME obtained from the column packed with the large aggregate is shown in Figure 3-16. The general shape of the data is closely matched by the model prediction. The simulated SEC, however, is displayed influenced by the data. This deviation is primarily a reflection of the value used for f , which in turn is a reflection of the assumption made to determine a value for f . Note that given the low value of α , the assumption of $k_1' = k_2'$ most likely did not influence the predicted results.

DATA SET 2

The final data set utilized is that of Ray and Ulrich (1947). Although their experiments were performed more than 50 years ago, this

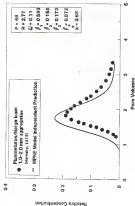


Figure 5.20 Substituted prediction of Benzophenone data (Comp-aggregates volume) obtained from eqn(5.16).

data set represents one of the most complete sets collected to date. They investigated the effect of flow velocity upon transport of the permeable lindane through columns packed with an aggregated soil. (Organized form) organic matter content = 2.1%. They were unable to associate lindane RTD with the LB model, and attributed this inability to the existence of heterogeneous diffusion (i.e., HED). The influence of flow rate on the transport of lindane is shown in Figure 5-12. The RTD for the higher-velocity ($v = 2.14$ cm/hr) experiment is retained lindane in comparison to the lower-velocity ($v = 1.44$ cm/hr) RTD. The tailing and lindane retention exhibited by the lindane data are evidence of a PDE-influenced system.

If lindane transport was affected by HED at the higher velocity, lindane transport should be as well. Based on the analysis of the previous experiments, it might be expected that a sorption-related nonequilibrium process could also have influenced lindane transport. To test this hypothesis, parameter values for the HED model were obtained independently as follows. The decay constant and α were obtained from a fit of the biexponential model to the high-velocity lindane data; the α value was corrected for differences in diffusion coefficients as described above. The retardation factor was calculated using a K_d value determined from a bench-laboratory experiment reported by Ray and Elrick (1987). To obtain values for the sorption-related parameters β and k_2 , the data obtained by Ray and Elrick (1987) from a bench sorption-desorption experiment was fit with the biexponential model (see Figure 5-12). The value determined for k_2 was used with eq. 5-12b to calculate a value for k_2' . Values for the β 's were calculated with eqs. 5-14 and

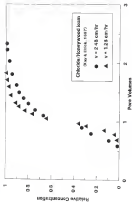


Figure 3-11 Chloride ions reported by Ray and Hurdle (1981)

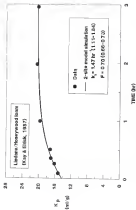


Figure 7.12 The parameter (b) (b) applied estimation of hard rejection-rate date of May and June (2011) provided with bootstrap model.

5-11, employing the assumption that $E = \beta$ and where β was determined from the chloride data.

The independent prediction obtained from the HFE model is compared to the high-velocity chloride FH in Figure 5-11. The HFE provided by the model describes the data relatively well. Some of the small deviation is probably a result of an accidental change in flow rate that was reported by Kay and Fickel (1961) to have occurred during the experiment. The parameter M^2 defined in eq. 5-12 can be used to evaluate MH validity for the nonpulsed/unpulsed convection process. Using values given in Figure 5-12 for the required parameters, a value of M is calculated for M^2 . Recall from the consistency analysis carried out that a value of M was determined as the limit at which the MH was valid, and that the HFE model reduces to the Klotzmann model in this situation. Given the large calculated M^2 value, the Klotzmann model should provide a prediction very similar to that provided by the HFE model, which in fact it does (HFE not shown). This experiment is a good example of a case where, although two convection processes were in operation, experimental conditions were such that only one of the two had a significant impact on solute transport. If, however, another experiment had been performed at even larger velocity (e.g., greater than 15 cm/hr), it might be expected that the Klotzmann model would no longer be able to adequately predict the outcome.

Discussion

A model was presented that explicitly accounts for multiple sources of convection. The performance of this model was compared to that

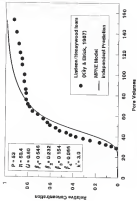


Figure 3.33. Independent prediction of Glaxo RT of Day and Error (RT) product with the fitted model.

of the aforementioned Hanes-Spence model. The formulation of the MPE model results in additional terms. Obviously, if values for these additional parameters are obtained through optimization, the MPE model should perform better simply because of the greater number of fitting parameters. Evaluation of model performance under these conditions is difficult. Reasonable model comparisons were made under the ideal condition for model evaluation, which entails that the number of fitting parameters has been reduced to zero, i.e., independent prediction. The results presented here show that the MPE model provides improved predictions in comparison to the Hanes-Spence model.¹

It must be stressed that the purpose of this work was not to obtain improved simulations of experimental data by increasing the number of model parameters. Rather, it was an attempt to improve the description of solute transport in natural systems by introducing a more complete representation of transport/absorption dynamics. The additional parameters introduced with the MPE model represent actual physiological processes and, thus, are not simply "adjustment factors". The ability to obtain values for the kinetic parameters of the MPE model from independent studies supports the claim that the parameters represent actual physiological processes.

Of course, additional parameters could be proposed with further elaboration of the present model. This process could be extended to the limiting case of a diffusion and/or mass-transfer process. Models based on such an approach may be able to simulate experimental data well, however, the number of parameters involved would greatly exceed our present capability to independently evaluate the processes.

represented by three parameters. Such models would, therefore, be restricted to operation in a collaboration mode. In the formulation of the MPM model, Wilson's paper was utilized in balancing the number of parameters with the capability to independently evaluate the underlying processes.

An empirical regression equation relating k to k_p was successfully used to evaluate values for the sorption-rate constant required in the MPM model. Further tests are required, however. Model results suggest that the relationship may serve useful in the investigation of sorption nonequilibrium. The MPM model was successfully used to provide completely-independent predictions of published data. Thus, to our knowledge, are the first such successful predictions for organic vapors. The success of the MPM model in independently predicting the data provides strong support for the validity of the conceptualization upon which the model is based.

Analysis of the published data would appear to suggest that under suitable conditions multiple processes can contribute to observed nonequilibrium. This potential would be especially significant at the field scale. Thus, when investigating or predicting solute transport, it is important to consider the possible existence of multiple sources of nonequilibrium.

CHAPTER 4 GRATE TRANSPORT AT THE FIELD SCALE

Introduction

The local equilibrium assumption (LEA) and the assumption of spatial homogeneity in spatial properties are the primary components of many models used to predict the transport of contaminants in groundwater. The validity of these assumptions has recently become a topic of considerable interest, especially in light of data showing deviations from that predicted with the simple models. Several processes can cause this modified behavior, including physical nonequilibrium, chemical nonequilibrium, heterogeneous diffusion, spatial variability in sorption coefficient, and spatial variability in hydraulic conductivity. While a significant amount of research on transport variability has been performed at the laboratory scale, little work has been done at the field scale.

Grate transport can be investigated employing either the balance or the Lagrangian approach. The nature of the transport variability displayed is, in part, dependent upon which of these two approaches is employed. For example, it has been well-documented that the temporal first moment of a solute pulse is independent of kinetic processes (Goreau and Roberts, 1987; Valocchi, 1988). The characterization of transport variability, esp., therefore, depend upon the approach

selected. Most of the work reported to date has involved either the second temporal moment or the first spatial moment. Under "ideal" conditions (e.g., 1D solid, homogeneous density, infinite transport) will be characterized) for example, by constant retardation factor (R) values and constant dispersion. The operation of natural phenomena can result in increased dispersion (larger second temporal moment) and time-dependent R values (time-varying first spatial moment).

Below transport may be investigated on several different spatial scales, including pore-scale, microscale (e.g., laboratory columns, small portions of an aquifer), mesoscale (often associated with larger portions of an aquifer) and gigascale (often associated with multiple wells or fractures). The degree of dispersion exhibited by a solute pulse at any given scale is a function of all the processes contributing to dispersion at that scale and at all smaller scales. Thus, the relative importance of the various phenomena that may contribute to dispersion is dependent upon the scale of interest. Applying the advective-dispersive transport equation in a solute front at a given scale results in the determination of a dispersion coefficient or dispersivity value (α) that is associated with that particular scale and that is representative of all processes contributing to the dispersion. If the dispersivity associated with hydrodynamic dispersion is taken as the base value, a value associated with all other processes and scales may be considered an effective α 's. Generally, these effective α 's decrease in magnitude with increasing scale. The interplay between the various length scales of the system of interest is a characteristic length associated with the controlling phenomena, length scale of

problem (length scale of mass transfer) greatly influences the observed α values.

Dispersion Mechanisms

The various phenomena that can cause conditions of residual solute transport for the Eulerian case are briefly discussed below. These factors can also cause nonideality for the Lagrangian case, however, other processes, in addition to those listed, may also cause nonideality for this case.

a) **Hydrodynamic dispersion**- dispersion in this case results from nonuniform velocity distributions at the intra-pore and inter-pore scales, the tortuous nature of the flow paths, and the existence of solute concentration gradients. Increased dispersion can result, for example, when the porous medium has a wide pore-size distribution.

b) **Physical nonequilibrium**- physical nonequilibrium (PNE) results from a heterogeneous flow domain at the microscopic level. Regions of lower hydraulic conductivity (S) within the flow domain act as sink/source components, with rate-limited diffusional mass transfer between these regions and the flow domain causing dispersion of the solute front. These sink/source regions can take various forms, including the internal porosity of aggregation, dead-end pores, the bulk matrix of fractured media, and the low K matrix-layers or laminae typically found in aquifers.

c) **Chemical nonequilibrium**- chemical nonequilibrium (CNE) occurs when the sorption process at the interface between the fluid and the sorbent surface is rate-limited. As discussed by Tomer and Lin

(1981), 1981 is generally not a dominant compensation mechanism for SSCs and hence, may usually be excluded from consideration.

ii) Interfacial diffusion: compensation associated with interfacial diffusion (IDD) results from the diffusional mass transfer of solute from the working surface into the lattice nuclei of the cathode. Considering signals arising from several surfaces on the two primary surfaces of interest, IDD may take one of two forms—interfacial mirror diffusion (IMD) or interfacial diffusion (IDD). IMD has been proposed as a cause for anodic compensation by several researchers (see section 5-3). IDD in systems involving clay minerals has been investigated by many researchers. However, IDD in systems involving typical anodic materials (e.g., quartz sand) has only recently received attention (cf., Bell and Roberts, 1987). Although both IMD and IDD involve a diffusional mass transfer mechanism, they may be considered as two different processes because 1) IMD influences both working and measuring electrodes, whereas IDD impacts only working electrodes; and 2) the mass transfer mechanism is quite different for the two processes.

iii) Vertical variations in anodic coefficient: The existence of vertical variations in anodic coefficient (k_a) can cause increased dispersion of working electrodes. Consider, for example, a porous medium comprised of several layers, each with a different k_a , but all with the same E . Solute is injected simultaneously into all layers. As transport proceeds, differential advancement of the solute fronts in each layer will occur because of the variations in permeability. This differential-front advancement will lead to the observation of increased

dispersion at a depth-integrated (or sampling-point) non-gradient of the injection point. In such situations, spatial variations in both E and E_p would be expected. The existence, and nature of, correlations between the two properties would be important for such cases.

This process has involved very little attention to date. Both van der Vaart (1981) evaluated the influence of spatially-variable oxygen exchange capacity (i.e., variable retardation) negatively correlated with E on solute transport in a simulated heterogeneous aquifer. They found dispersion to increase as the variance in retardation increased. However, they concluded that this effect would be of secondary importance in comparison to the effect of spatial variability in E . The influence of a spatially-varying E on solute transport in a homogeneous aquifer was investigated with model simulations by Jirassak and Inghary (1982). Effective dispersion coefficients exhibited scale-dependent asymptotic oscillatory, or negative values, depending on the configuration of the retardation field. This mechanism was proposed as the cause of the enhanced dispersion exhibited by lithium in comparison to bromide, in a recent natural gradient experiment at Cape Cod, MA (Kavanaugh et al., 1981, 1982).

1) Nonequilibrium nonequilibrium results from spatial variations of E in the flow domain of the microscopic scale (i.e., heterogeneous aquifer). This process has been the focus of much research. Since that nonequilibrium is distinct to the physical nonequilibrium that results from the influence of lackness of varying E , they are discussed above in (a). In fact, the mechanism producing the two phenomena is the same, the only difference being one of scale. The two may be operationally

differentiated by the extent of spatial resolution of the sampling device employed to measure solute concentrations. The increased dispersion resulting from vertically-averaged sampling in heterogeneous systems (i.e., a wellboring will encounter over a substantial portion of an aquifer) is considered macrodispersion. Conversely, the increased dispersion observed at the scale of a single, discrete pore within an aquifer is considered the realm of PDE. Obviously, the use of discrete, multi-level sampling devices is necessary to measure both PDE. Both devices have an effective vertical sampling zone of approximately 1 to 10 cm (cf., Harvey et al., 1988a).² Hence, PDE-related dispersion in aquifer systems may be defined as that observed at the centimeter scale. (i.e., multi-pore scale) whereas macrodispersion is observed at the megameter scale.

The difference between the two phenomena may be illustrated with the data reported by Hickox and Reich (1981) - a dispersivity of 8.555 cm representing the contribution of hydrodynamic dispersion, was measured from solute displacement through columns packed with aquifer material. At the scale of a discrete level within the aquifer, a dispersivity of 8.7 cm was obtained for data collected with multi-level point sampling of a field tracer experiment. The difference between this value and the laboratory value represents the effect of PDE. The "full-aquifer" dispersivity of 94 cm, derived from a small two-well tracer test with depth-integrated sampling, represents the effect of macrodispersion.

The α values obtained at different scales may be compared to assess the relative significance of the various dispersion mechanisms. Both in

evaluation is performed with a uncertainty which processes are likely to predominate at the field scale.

Data from Baskin et al. (1994), Liu et al. (1993b), Pichon and Griseb (1991), and Gelwick and Watzinger (1994) show that PH-induced anisotropy can result in roughly an order-of-magnitude increase in dispersivity. Data from Pichon et al. (1991), Brierley et al. (1994), and Liu et al. (1993) show that sorption-induced anisotropy (e.g., 1000–100) can also result in roughly an order-of-magnitude increase in dispersivity. This order-of-magnitude effect is also demonstrated by dispersivity values calculated at different scales for two aquifer systems, Jordan and Dutch River. In a value of 1.0 m, representing the combination of hydrodynamic dispersion, was obtained for a packed column of Jordan sand. A value of approximately 4.5 m, representing the combination of sorption anisotropy-induced dispersion in addition to hydrodynamic dispersion, were obtained by fitting the A-D model to the RTDs of two RTDs obtained from piston displacement through Jordan sand. A value of approximately 5 m were determined for RTDs obtained at individual levels for a field-scale experiment. Extrapolated with multi-level coupling devices at the Jordan site. This dispersivity represents the PH-induced dispersion associated with the effects of the clay-lapine clay matrix in the aquifer, as well as hydrodynamic dispersion and sorption anisotropy-induced dispersion (see, for example, Gelwick (1994) for a discussion of the heterogeneity of the Jordan aquifer). Similar values for the various processes were obtained by Pichon and Griseb (1991) and Pichon et al. (1991). The order-of-magnitude impact associated with the macroscopic dispersion

processes (e.g., PBL, IBL, OBL) could be significant for systems where the data are obtained with multi-layered sampling techniques. However, if vertically-averaged samples are taken, these order-of-magnitude effects are likely to be small compared to the impact of stratification. For example, "macroscopic" dispersivity values of approximately 50 m, representing the small portion of the domain needed to think the macro-gradient solute transport experiments are performed, were obtained by Ralston (1984) and Freyberg (1984). Full-scale macrodispersivity values of 10-50 m were determined from analyzing the transport of "bank" solutes in the Rhine aquifer (Aghaie et al., 1981). The two to three order-of-magnitude difference in values emphasizes the relative effect of macroscopic vs. mesoscopic dispersion processes.

The conclusion that macroscopic dispersion predominates over such processes as PBL, IBL, and OBL at the field-scale is supported by a theoretical analysis of the relative contributions of sorption kinetics and aquifer heterogeneity to contaminant dispersion reported by Yeh and Cohn (1984). His analysis indicated that "kinetic effects may not be important for modeling depth-averaged plume behavior in highly heterogeneous systems." A similar conclusion was reached by Hsu et al. (1984). Based on the interpretation of experimental results obtained at microscale and macroscale scales, they concluded that PBL processes would most likely not be important, in comparison to macrodispersion, at the field scale. The predominance of macrodispersion over other processes at the field scale is also suggested by the work of Hsu and coworkers (Hsu et al., 1982; Hsu et al., 1983; Hsu et al., 1984, 1984), who have shown that the majority of the dispersion observed in

current data they have evaluated results from vertical distributions of R values.

Field-Scale Transport Experiments

A recently completed in-situ-ground field experiment in a sand aquifer at the Canadian Forces Base, Halifax, Ontario (Mortley et al., 1984a; Roberts et al., 1984; Davis et al., 1984; Kubiak, 1984; Poretsky, 1984; Golan and Roberts, 1984) provides an excellent case study of organic contaminant transport at the field scale. As this is the first comprehensive field experiment specifically designed to evaluate processes affecting the transport of organic solutes in an aquifer system, valuable information could be expected from the results. An evaluation of the results with respect to sorption, sorptivity and dispersion is presented below. Data obtained with an isolation approach will be discussed first, followed by a discussion of data obtained with the Lagrangian approach.

Isolation Approach

Breakthrough curves (BECs) for sorbing (chloride) and non-sorbing (sodium nitrochloride, bromide, and hexachlorobenzene (PCE)) solutes obtained at a specific x, y, z coordinate were reported by Selgey and Roberts (1984). The authors fitted two theoretical models, representing PDEs in the data. Inspection of their Figures 1 a, b, c and 2 a, b, c shows that, while the theoretical models provided a generally good fit to the data, the tailing exhibited by the BECs of the sorbing solutes was more extensive than that predicted by the models. Conversely, the models did provide very well the tailing of the non-sorbing solutes, which

was less extensive than that of the working solution. This behavior, where the EPR model completely simulates a EPR of a nonworking solution but not that of a working solution, suggests the relevance of an additional, complex-related, nonequilibrium mechanism. Fitting a model that includes a single nonequilibrium term to data influenced by one or more nonequilibrium processes results in the determination of a lumped or global kinetic parameter. While this approach may be adequate for simulating the EPR, it is not conducive to process-level investigation of complex dynamics.

To further investigate the apparent nonequilibrium exhibited by the data of Odeh and Lebrun (1981), the multi-process nonequilibrium model developed in section 5 was used to simulate the EPR of EOR (see Figure 6-1). This model accounts for the presence of one nonequilibrium mechanism associated with EOR, and it is noted that any dependent set of several complex-related processes (e.g., IOR, EOR, species variations in viscosity) in displacement drive the model requires 8 parameters: F , β , α , k^* , β_1 , β_2 , β_3 , and β_4 (each parameter is defined below). The α value, which is the pseudochemical rate parameter (i.e., Hammett number) representing the effect of EOR, was determined by fitting a bicontinuous model to the 6E EPR. This α value was adjusted to take into account the difference in liquid diffusion coefficients for Cl^- and EOR. The retardation factor value was calculated using a partition coefficient determined from a batch isotherm reported by Gortie et al. (1981). The Péclet number (Pe), representing hydrodynamic dispersion, is taken from values obtained from column experiments.

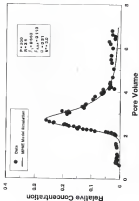


Figure 4-1. Comparison of simulated (solid line) and measured breakthrough curves for Pb at the bottom of the column (data were from Smith and Roberts [2004]).

utilizing Jordan aquifer material reported by Lee et al. (1980). The values for k^* (bubblular number representing the second, sorption-related nonequilibrium mechanism) and β_1 (the fraction of sorption associated with instantaneous sorption) are fit values. The values for k_1 , k_2 , and k_3 (fractions of rate-limited sorption) were arbitrarily set equal such that the simulation is, in effect, a two-parameter fit (the sum of the four β 's equals one).

From the k^* value of k , a dimensional first-order rate constant (k_4) of 0.0013 hr^{-1} is calculated. This value can be compared to values that might be expected from various sorption-related nonequilibrium mechanisms. The equation presented in section 4-3 may be used to estimate k_4 values for systems influenced by DMS. Using the k_4 value reported by Gurrie et al. (1986), a k_4 value of approximately 1 hr^{-1} is estimated. It is apparent that the estimated value is much larger than 0.0013 hr^{-1} , which suggests that DMS is not an important mechanism on the scale of this experiment. Gurrie (1984) reported a relaxation time for diffusion of DdC in for a batch uptake experiment involving Jordan aquifer material and PCB. Using this value, k_4 values of roughly 0.1 to 0.51 hr^{-1} can be estimated, depending on the equation employed. These values may represent the combined effects of DMS (diffusion of solute into microsporous void spaces, as proposed by Hill and Roberts (1987)) and DMS. Comparing these k_4 values to 0.0013 hr^{-1} shows that the former are one to two orders-of-magnitude larger. This suggests that, while the processes represented by the batch experiment (k_4 , DMS) may contribute to the nonlinearity exhibited by the PCB BTC, this contribution is not significant enough to explain all of the

instability. Thus, another excitation-induced mechanism appears to be involved.

As mentioned above, CRT is unlikely to be involved in this system. With PSE, LQAS, DIS, and CRT removed for, the only remaining mechanism is vertical variations in E_y . The E_y values for PSE were found to vary over nearly an order-of-magnitude among 35 cm depth increments in ± 1 s (interval of the Barker amplifier (Parker et al., 1988)). The existence of an enhanced-dispersion component resulting from such a variation is quite probable. Based on the above discussion, it appears that spatial variability in both E and E_y may be responsible for the modified behavior exhibited by the data of Cole and Roberts (1988).

Comparing the magnitude of the nonlinear modes associated with the two processes, obtained from fitting the dual-process model to the PSE data, can provide some indication of their relative significance. The value for α (0.15), representing PSE, is an order-of-magnitude smaller than the value for β' (1.5), which represents the effect of vertical variations in E_y . This suggests that PSE has a somewhat greater role in producing the variability exhibited by the writing system. This would be in accordance with the conclusion of Smith and Roberts (1981), discussed above. The relative insignificance of the other factors (e.g., hydrodynamic dispersion, DIS, CRT) is in agreement with the discussion presented in section 3.

Interregion approach

Synaptic coupling of the constituent gives in the α - β gives was also performed during the Barker Field experiment. Analysis of the data

revealed that calculated correlation factor values increase with time (Roberts et al., 1984). The temporal increase in sorption then is explained by this behavior and is explained by one or more of the following mechanisms: 1. a directional trend of increasing sorption affinity of the spider within the cylinder with the diameter of glass vials; 2. nonlinearity (Fick) resulting in an increasing k as concentration decreases with time as a result of phase spreading; 3. anisotropy resulting in the existence of a preferred sorbed component; 4. differential rates of transformation processes such that solute concentrations at the leading edges of the phase are distributed to a greater extent than at the trailing edges; 5. Fick; 6. GBE; 7, 10 and 8. spatial variations in D_p .

No apparent trend was observed in the average sorption characteristics of the spider within in the horizontal direction (Shenoy et al., 1984). Corbin et al., (1984) have shown that the sorption isotherms for the compounds involved are approximately linear, and exhibit no significant hysteresis. A long-term (30 day) desorption experiment performed by Shenoy (1984) exhibited only slight hysteresis and no evidence of the existence of an irreversibly-sorbed component. There was no evidence of greater solute disappearance at the leading edges of the phase (Roberts et al., 1984). These results eliminate alternatives 1 to 4 from consideration as potential major contributions to the observed non-linearity. Alternatives 4 and 7 may be considered as relatively insignificant in this case, as discussed in the previous section. Thus, FBE, resulting from the spatial variability in k , and

vertical variations in E_p are the only remaining probable candidate mechanisms for the observed anisotropic conductivity.

The existence of anisotropic heterogeneity in E at the border site is well documented (Gosling, 1966). The influence of this heterogeneity on the transport of searching tracers has been investigated (Hollay, 1978; Paschke, 1986). The enhanced dispersion resulting from this heterogeneity would also affect the transport of the seeking solutes. The question is, is the effect of this process (HE) great enough to explain all of the residual behavior exhibited by the seeking solutes? Selzer and Roberts (1988) simulated the spatial first moment data obtained from the syringe sampling with a model representing physical mass transfer in a layered system (Selzer, 1982). If HE were the primary mechanism responsible for the residual behavior (temporal variation in E) exhibited in the experiments, the simulations produced with this model should well-predict the data. In fact, the model simulations overpredicted the degree of plate broadening (i.e., the amplitude of the increase in E values). This provides evidence that an additional, conductivity mechanism is involved. Inspection of Figure 8 in Roberts et al. (1988) shows that the amplitude of the temporal increase in E increases with the sorptivity of the solute. This would suggest that the additional conductivity mechanism is sorption-related. Given the discussions presented above and in the previous section, it appears that this mechanism may be vertical variations in E_p .

A Model for Field-Scale Solute Transport

The literature presented above demonstrates that solute transport at the field scale is influenced by multiple interacting processes and that the impact of these processes is scale-dependent. A model may account for this if it is to provide adequate simulations of transport under these conditions. To address this issue, a model that includes advection, scale-dependent, nonlinearity was developed. The model explicitly accounts for the following processes: hydrodynamic dispersion, physical nonequilibrium, sorption nonequilibrium, spatially-variable hydraulic conductivity, and spatially-variable equilibrium-sorption isotherm.

The model is based on the model presented by Gelhar (1980). This model utilizes solution to Laplace's equation to simulate the flow for flow mapping. This approach is both more efficient and is much easier to modify to incorporate additional components. It is, however, limited to linear problems. The model as presented by Gelhar (1980) accounts for spatially-variable hydraulic conductivity (K). This may be done with one of two approaches: deterministic, where a K value is specified for each element, or stochastic, where statistical parameters representing the K field are employed.

The model of Gelhar (1980) was modified to incorporate spatially-variable equilibrium-sorption isotherm and nonequilibrium sorption. The formulation presented in Figure 3-4 was utilized for the 2-D case. The modified model, then, can account for all of the dispersion mechanisms discussed in the previous section. This model should be very useful for investigation of the relative importance of the different

nonadiabatic processes that not affect electron transport in the silicon

The static effect for nonadiabatic can be illustrated with the following two examples. For the first example data for the transport of electrons (^{28}Si) through a metal semiconductor separated by SiGe at 4 K (199) was used. The semiconductor consisted of three horizontal layers where the middle layer was a metal and the top and bottom layers were the same alloy. A metal accounting for effective transport in the metal layer, diffusion mass transfer in the alloy layers, and local equilibrium generated interaction in all layers was used to describe the experimental. The Kane Kane et al., (1993). The authors could derive a false conclusion of the data only by optimizing the values for β , the β value for the alloy was much smaller than that based on the bulk parameters. From this it may be suggested that a third nonadiabatic process, namely carrier nonadiabaticity is involved in addition to the vertical spatial variability of electronic conductivity and of the injection coefficient.

To test this, the Kane model was used to calculate the ^{28}Si EPR (see Figure 4-3). Values for β (100) and α (3.31) were obtained by fitting the Kane model to a standard EPR, a value for β for the silicon percent silicon ($\beta = 1$, weighted average β) was obtained using the β_0 values obtained from the bulk parameters. The values for $\beta_0 = \beta_1$ (3.3) and $\beta_0 = \beta_2$ (3.4) were based on the mass fractions of the two types of materials (GaAs, SiGe). This, in essence, is employing the assumption that the metal layer is acting as a mobile domain and that the alloy layers are acting as immobile domains. Hence, the mobile-immobile mass transfer represented by α is used to account for the spatially-variable

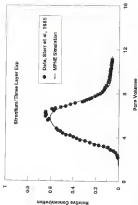


Figure 3.4. Simulations of Storr et al. (1989) for 1000 particles with MFM2 model, show excellent agreement with measured for physical sorption/desorption isotherms (variable hydraulic conductivity, spatially variable sorption intensity) and complex competition.

hydraulic conductivity. The influence of the spatially-variable sorption coefficient ($K_d = 1.0$ for the sand and $21.0 \text{ m}^3/\text{kg}$ for the silt) can be accounted for by multiplying the value of α with the factor $K_{\text{sand}}/K_{\text{silt}}$. This procedure was done to obtain the α value of 0.07. The value for K' (0.001) was spinelized. The value for k_d calculated from K' is 0.002 hr^{-1} . This value is close to a value of 0.002 hr^{-1} reported for the non-limited sorption of aluminum in sphyerulites (Salayeh et al., 1992). This does would seem to suggest that chemical nonequilibrium was an important factor for this system.

For the second example, simulations were produced with the model presented in this section. The case used was that of a randomly heterogeneous hydraulic conductivity field, where the realization was produced with the turning-band technique (Isaiah, 1989). The statistical properties employed to develop the realization were based on values reported by Isaia (1989) for the Boston aquifer. Sorption was constrained to be non-limited; the values for K_d and k_d were selected to represent those obtained for the sorption dynamics of tetrachloroethene in the Boston aquifer material (see the discussion associated with Figure 4-4). The relative importance of nonequilibrium sorption was investigated by performing two simulations, one with local equilibrium assumed and one with non-limited sorption included (see Figure 4-3).

Comparing the two plumes. It appears that the inclusion of nonequilibrium sorption did not significantly impact plume development. This is not surprising given that the characteristic time of reaction used for this example is smaller than the effective residence time of

the solute. Thus, sorption nonequilibrium may not be an important process affecting the transport of solute under relatively low velocities ($U < 1$ cm/sec), typical of groundwater at the field scale. This is not to say, however, that nonequilibrium may not be important at the field scale under high-velocity conditions, such as those occurring during the flushing of contaminated aquifers.

SUMMARY

In Chapter 1, experimental methods for investigating the sorption kinetics of organic chemicals were developed and evaluated. It appears that the gas-purge technique is best for investigating the sorption dynamics of volatile organic chemicals in diffusion/lamination systems and in high organic carbon soils systems. The design used herein has limited usefulness, however, for low organic carbon systems (e.g., aquatic materials). The static displacement technique seems well suited for investigating sorption and transport in low organic carbon systems. The gas-purge and static displacement techniques were shown to provide comparable results for the determination of kinetic parameter values. Thus, two techniques may therefore be used to complement each other; the choice of which to use being determined by the nature of the system of interest.

A modified form of the static displacement technique, called flow interruption, was developed. This technique should be useful in estimating the influence of parameter value determination. The flow-interruption method may also prove useful in such large-scale applications as remediation of contaminated aquifers. The methods presented in Chapter 2 were employed to investigate the mechanisms involved in nonpollutant sorption.

Three objectives were pursued in Chapter 3. The first objective was an investigation of the influence of various sediment structures on

orption kinetics. A log-log linear relationship was discovered between the kinetic sorption constant and the equilibrium sorption constant; this relationship was quantified. This relationship was shown to be useful in providing estimates of values for the sorption rate constant.

The influence of various molecular structure on sorption kinetics was recognized to be important under certain conditions. The sorption of so-called amphiphilic chemicals (e.g., those containing reactive functional groups) was found to be much more complicated than that of the hydrophobic chemicals. This was suggested to result from specific interactions involving between functional groups of the sorbate and the sorbent. Thus, the presence of reactive and/or polar functional groups can significantly affect sorption kinetics. Commonly, the influence of molecular structure on kinetics appears to be of secondary importance for hydrophobic chemicals. For example, the k_p/k_d relationship for a homologous series of benzenes, naphthalenes, and anthracenes was found to be essentially the same as that exhibited by two other series (di, tri, and tetra chlorobenzenes and chloro, dichloro, trichloro, and tetrachloro benzenes).

An investigation of the influence of sorbate structure on the equilibrium sorption of organic solutes was the second objective of Chapter 4. A model describing a significant relationship between the sorption rate constant and volume fraction sorbent was developed. Experiments were performed to evaluate this model. The results appeared to support the validity of the proposed model. It was also shown that results obtained from experiments performed with solid sorbents could be

would be suitable values for the sorption rate constant in aqueous systems. The use of mixed solvents should prove very useful in studying the solvent constraints associated with performing kinetic experiments with highly hydrophobic chemicals.

Identification of the mechanism responsible for sorption nonequilibrium was the third objective of Chapter 5. Diffusive mass transfer of solute within the organic matter component of the system was suggested to be the most probable cause of sorption nonequilibrium for hydrophobic organic chemicals for most cases, based on an analysis of data presented in the literature. The results of experiments presented in this work supported this hypothesis. For example, the degree of nonequilibrium was observed to decrease significantly when the organic matter content of a soil was reduced by passage through a filter. This would suggest that the mechanism responsible for rate-limited sorption involved the organic matter. The results of the sorption experiments with naphthalene and the experiments with the aliphaticenes are very suggestive of a mechanism involving diffusive mass transfer within a polymeric structure as being responsible for the observed nonequilibrium. The results of the kinetic and partition experiments are also suggestive of the involvement of this type of mechanism.

A model for simulating solute transport under conditions of multiple sources of nonequilibrium was developed and evaluated in Chapter 6. This model will be useful for investigating and modeling solute transport in complex systems where nonequilibrium may be caused by one or more processes. It will also be useful for elucidating the conditions under which the local equilibrium assumption may be valid.

A model describing solute transport at the field scale, where nonideality may result from several processes (hydrodynamic dispersion, physical nonequilibrium, sorption nonequilibrium, spatially-variable hydraulic conductivity, and spatially-variable sorption constant) was presented in Chapter 2. This model, along with the model presented in Figure 1, was used to simulate several cases of solute solute transport that have been reported in the literature. The results of these simulations suggest that the process(es) responsible for nonideality are scale dependent. At the microscale scale (e.g., laboratory), nonequilibrium sorption may be the predominant nonideality process. At the field scale, nonideality associated with spatially-heterogeneous soil/soilwater properties (e.g., hydraulic conductivity, equilibrium sorption constant) may predominate.

Bathylagurus

Depth (m) Relative
Concentration

1	414879	0
2	415109	0
3	417174	0
4	447794	0
5	448373	0
6	448408	0
7	449748	0
8	449717	0
9	450445	0
10	451141	0
11	452458	0
12	453314	0
13	453947	0
14	4539138	0
15	454110	0
16	454191	0
17	454119	0
18	454197	0
19	454197	0
20	454197	0
21	454197	0
22	454197	0
23	454197	0
24	454197	0
25	454197	0
26	454197	0
27	454197	0
28	454197	0
29	454197	0
30	454197	0
31	454197	0
32	454197	0
33	454197	0
34	454197	0
35	454197	0
36	454197	0
37	454197	0
38	454197	0
39	454197	0
40	454197	0
41	454197	0
42	454197	0
43	454197	0
44	454197	0
45	454197	0
46	454197	0
47	454197	0

Bathylagurus

Depth (m) Relative
Concentration

1	414879	0
2	447794	0
3	448373	0
4	448408	0
5	449748	0
6	449717	0
7	449717	0
8	449717	0
9	449717	0
10	449717	0
11	449717	0
12	449717	0
13	449717	0
14	449717	0
15	449717	0
16	449717	0
17	449717	0
18	449717	0
19	449717	0
20	449717	0
21	449717	0
22	449717	0
23	449717	0
24	449717	0
25	449717	0
26	449717	0
27	449717	0
28	449717	0
29	449717	0
30	449717	0
31	449717	0
32	449717	0
33	449717	0
34	449717	0
35	449717	0
36	449717	0
37	449717	0
38	449717	0
39	449717	0
40	449717	0
41	449717	0
42	449717	0
43	449717	0
44	449717	0
45	449717	0
46	449717	0
47	449717	0

Erichsenprobe

Form, Volumen	Relative Densität
0 440181	0
1 010034	0 000180
1 100000	0 100434
1 140004	0 440001
1 110003	0 440004
2 010004	0 100004
2 140004	0 100001
3 100001	0 000007
4 100007	0 100000
5 040001	0 040001
6 000000	0 000000
7 10	0 000000
8 040004	0 010000
10 00000	1
11 00000	1
12 04000	0 000000
13 00000	0 040000
13 00000	0 440007
13 00000	0 440007
13 10000	0 100000
14 000	0 100000
15 04000	0 010000
16 10000	0 000000
16 10000	0 010000

1.1.1.1. Lössschichten

Form, Volumen	Relative Densität
0 440180	0
1 010004	0
1 000000	0 100000
1 000000	0 100000
11 01000	0 100000
12 00000	0 100000
13 00000	0 100000
14 00000	0 100000
15 00000	0 100000
16 00000	0 100000
17 00000	0 100000
18 00000	0 100000
19 00000	0 100000
20 00000	0 100000
21 00000	0 100000
22 00000	0 100000
23 00000	0 100000
24 00000	0 100000
25 00000	0 100000
26 00000	0 100000
27 00000	0 100000
28 00000	0 100000
29 00000	0 100000
30 00000	0 100000
31 00000	0 100000
32 00000	0 100000
33 00000	0 100000
34 00000	0 100000
35 00000	0 100000
36 00000	0 100000
37 00000	0 100000
38 00000	0 100000
39 00000	0 100000
40 00000	0 100000
41 00000	0 100000
42 00000	0 100000
43 00000	0 100000
44 00000	0 100000
45 00000	0 100000
46 00000	0 100000
47 00000	0 100000
48 00000	0 100000
49 00000	0 100000
50 00000	0 100000
51 00000	0 100000
52 00000	0 100000
53 00000	0 100000
54 00000	0 100000
55 00000	0 100000
56 00000	0 100000
57 00000	0 100000
58 00000	0 100000
59 00000	0 100000
60 00000	0 100000
61 00000	0 100000
62 00000	0 100000
63 00000	0 100000
64 00000	0 100000
65 00000	0 100000
66 00000	0 100000
67 00000	0 100000
68 00000	0 100000
69 00000	0 100000
70 00000	0 100000
71 00000	0 100000
72 00000	0 100000
73 00000	0 100000
74 00000	0 100000
75 00000	0 100000
76 00000	0 100000
77 00000	0 100000
78 00000	0 100000
79 00000	0 100000
80 00000	0 100000
81 00000	0 100000
82 00000	0 100000
83 00000	0 100000
84 00000	0 100000
85 00000	0 100000
86 00000	0 100000
87 00000	0 100000
88 00000	0 100000
89 00000	0 100000
90 00000	0 100000
91 00000	0 100000
92 00000	0 100000
93 00000	0 100000
94 00000	0 100000
95 00000	0 100000
96 00000	0 100000
97 00000	0 100000
98 00000	0 100000
99 00000	0 100000
100 00000	0 100000

Random

Base Values	Relative Concentration
0 507234	0
0 779950	0.000251
0 834883	0.007377
1 000219	0.100337
1 148663	0.308738
1 394871	0.496238
1 668037	0.490365
1 969819	0.456258
2 047070	0.418528
2 147977	0.386664
2 414139	0.356238
2 695021	0.470070
3 104204	0.696481
3 176	0.388588
6 130756	0.612581
6 665488	0.654294
6 610700	0.654294
6 616676	1
6 670000	1
6 661496	0.610700
6 664766	0.768548
7 000800	0.218508
7 082000	0.764488
7 201640	0.310000
7 575440	0.110000
7 651700	0.617700
8 110	0.610500
8 660000	0.610000
9 000216	0.600000
9 704014	0.654014
10 00000	0.671111
10 69079	0.607407
11 66134	0.600000
11 66090	0.607000
11 66000	0

Self-Exciting

Base Values	Relative Concentration
50 01660	0
60 00106	0.007088
70 34480	0.048804
80 81440	0.048804
90 80076	0.057500
98 61108	0.321070
100 4080	0.710000
110 1850	0.348708
118 0807	0.387068
128 6007	0.668900
146 0914	0.697008
160 5006	0.654700
178 0480	0.660000
184 0908	0.656000
211 1680	1

REFERENCES

- Engley, J. V. An evaluation of the attachment mechanisms for dissolved anionic hydrocarbons from a gasoline source to a sandy surficial aquifer. Ph.D. Diss., State Florida, Gainesville, FL, 1983
- Jacobowitz, R. A., Wenz, F. B., McElroy, R. B. and Rogers, T. R. Air-water partitioning coefficients of organics in dilute aqueous solutions. *J. Resour. Water*, 19, 15, 1988
- Kubi, J. R., and Kubiak, J. Direct comparison of kinetic and local equilibrium predictions for solute transport affected by surface reactions. *Water Resour. Res.*, 19, 458, 1983
- Leahy, R. W., White, F. L., and Kothberg, F. Adsorption of organic hydrocarbons by noncrystalline soils of pH and chemical character of adsorbate. *Soil Sci. Soc. Am. J.*, 32, 333, 1968
- McLennan, J., Kothberg, F., Lee, F. B. C., and Brown, R. B. Field study of solute movement in a highly aggregated soil with interrelated flooding. *Water- & Air Pollution Qual.*, 2, 345, 1979
- Neil, W. F., and Roberts, P. V., Rate limited sorption of halogenated aliphatic onto sandy aquifer material- Experimental results and implications for solute transport. *Env. Sci. Tech.*, 1985
- Neil, W. F. and Roberts, P. V., Sorption kinetics of synthetic organic chemicals in sandy aquifer material. *Proc. Qual. Res. Soc. South Afr.*, Durban, 22-24-25, 1987
- Reynolds, R. and Roberts, P. Adsorption and water flow in soils. *Water Resour. Res.*, 18, 1343, 1982
- Rigger, J. V., and Williams, R. B. Diffusion effects in saturated and unsaturated porous materials. *J. Geophys. Res.*, 69, 1983, 1984
- Rigger, J. V., and Williams, R. B. Flexible diagenesis: A behavior of organic- *Soil Sci. Soc. Am. Trans.*, 78, 125, 1984a
- Rigger, J. V., and Williams, R. B., Some comments on molecular diffusion and hydrodynamic dispersion in porous media. *J. Geophys. Res.* 47, 3458, 1982b

- Higgin, J W., and Nielsen, E E., *Microbe-Macroinvertebrate Exchange Processes*. Soil Sci. Soc. Am. Trans., 27: 423, 1963.
- Keeney, J J & J., and van der Pui, L J J. Tests of some aspects of a model for the adsorption/desorption of herbicides in field soils. *Soil App. Biol.*, 4, 445, 1964.
- Keeney, J J & J., and van der Pui, L J J., Modeling adsorption/desorption kinetics of pesticides in a soil suspension. *Soil Sci.*, 146, 211, 1969.
- Keeney, J J & J., van der Pui, L J J., and Smith, J B., Field test of a mathematical model for the equilibrium transport of pesticides in soil. *Soil Sci.*, 88, 167, 1967.
- Leachman, R C., Smith, A L., Campbell, W L., West-Graham, P., and Lee, P E C., Sorption equilibrium during solute transport. *J. Geom. Spect.*, 2: 301 1968.
- Leach, E A., and Rice-Sa G., Accelerated herbicide leaching resulting from preferential flow phenomena and its implications for ground water contamination. pp 443-455. In: *Proc Conf on Groundwater Ground Water Toxicity*, Phoenix, AZ, 28-31 Oct., 1966, Nat. Water Well Assoc. (Dallas, TX).
- Lloyd, E. A. Adsorption of solubilized phenols by soil. *Soil Sci.*, 126: 187, 1961.
- Lloyd, E. A. KENNEDY, E. R. Reactions of alkyphenols in soils. *Agrochim. Acta*, Amer. Soc. Agrochim., Madison, WI, 277 1967.
- Lyons, E. The diffusion model of longitudinal mixing in beds of silica. *Langmuir Chem. Eng. Sci.*, 17: 723, 1962.
- Lyons, E. E., Lyman, E. R., and Orr, F. R. Mixing during single-phase flow in reservoir rocks. In: *Reservoir Characterization*, Lake, L. G. J., Houston Texas: Elsevier, NL, 1964.
- Lyons, E. E., and Orr, F. R. E. Sorption equilibrium during organic contaminant transport in porous media. ORG Critical Reviews in Review. *Chem.*, 23: 23, 1970.
- Malik, E. Kinetics of ion exchange in soil-suspension system. III. Differential ion exchange kinetics of Pb^{2+} ions in humic acid and peat. *J. Soil Science*, 26: 1129 1974.
- Malik, E., Schellig, W., and Hesse, E. Kinetics of ion exchange in soil-suspension system. IV. Adsorption and desorption of Pb^{2+} , Ca^{2+} , Mg^{2+} and Cu^{2+} by peat. *J. Soil Science*, 17, 21 1976.
- Perkins, E., Hayes, R., and Greenland, E. J. Adsorption. In: *The Chemistry of Soil Processes*, Greenland, E. J., and Hayes, R. (eds.) Wiley, NY, 1981.

- Brown, I. B., Noyes, R. B. B., and Draney, R. Some physical-chemical interactions of pyrope with soil organic materials and metal compounds. *Water Res.*, 15, 67, 1979.
- Cannon, J. B., and Elerts, S. Descriptive-dispersive solute transport with a combined equilibrium and kinetic adsorption model. *Water Resour. Res.*, 23, 181, 1977.
- Chen, S. T., Roberts, L. J., and Freund, F. H. A physical concept of soil-water equilibria for organic organic compounds. *Science*, 206, 871, 1979.
- Craine, J. T., and Elertman, S. W. Desorption kinetics for selected PCB congeners from river sediments. *J. Environ. Hydraul.*, 1, 281, 1984.
- Crooks, R. B., and Smith, R. J. Bond-end pore volume and dispersion in porous media. *Can. J. Soil Sci.*, 4, 72, 1964.
- Draney, R. B., Johnson, R. A., and Brown, A. L. Effects of particle size distribution on adsorption kinetics in stirred batch systems. *Chem. Eng. Sci.*, 34, 1505, 1980.
- Frimanster, J. C., Neuman, R. J., Soper, S. G., Greville, J. L., and Frimman, G. Transport of organic compounds with saturated groundwater flow: Model development and parameter estimation. *Water Resour. Res.*, 18, 571, 1982.
- Garcia, G. E. Sorption of halogenated organic solutes onto aquifer materials: Comparison between laboratory results and field observations. *Engineers Thesis, Stanford Univ., Palo Alto, CA*, 1984.
- Garcia, G. E., Roberts, P. F., and Schindler, R. A natural gradient experimentation solute transport in a sand aquifer, a. Sorption of organic solutes and the influence on mobility. *Water Resour. Res.*, 20, 3059, 1984.
- Harshbarger, P. F. Desorption flow systems. *Chem. Eng. Sci.*, 3, 1, 1980.
- Neuman, J. B., and Chang, S. E. Transport of glaucous in relation to soil physical conditions and pore water velocity. *Soil Sci. Soc. Am. Res.*, 34, 287, 1970.
- Neuman, J. B., Black, C. E., and Harshbarger, P. F. Influence of water flow and porous material on the movement of selected hydrophobic. *Soil Sci. Soc. Am. Res.*, 33, 128, 1969.
- Rees, R. A. A mathematical model for dispersion in the direction of flow in porous media. *Soil. Phys. Eng. J.*, 3, 49, 1982.
- Roberts, P. F., and Draney, R. In: Chemical Geochemistry. Wiley, J. P., and Draney, R. (eds.) Academic Press, New York, 1984.

- Delmon, F., and Wieringa, P. J. Solute transfer through columns of glass beads. *Water Resour. Res.*, **10**, 105, 1974.
- Engels, E. F., and Schmalz, T. R. Air-water-soil vapors transfer. *Water Resour. Res.*, **19**, 179, 1983.
- Healy, P. J., and Amundson, R. H. Mechanisms of adsorption. IV. Effects of intraparticle diffusion in agitated batch systems. *J. Phys. Chem.*, **54**, 766, 1950.
- Hyman, J. C. E., Cherry, J. A., Fawcett, R. B., and Pryor, J. B. Migration of contaminants in groundwater in a landfill: a case study. 3. Solutes as an indicator of dispersion and recharge. *J. Hydrol.*, **73**, 31, 1983.
- Klick, J. E., Erb, R. F., and Knap, R. E. Applications of chloride displacement techniques to wells. *Water Resour. Res.*, **1**, 317, 1965.
- Klick, J. E., and French, L. R. Chloride displacement technique on disturbed and undisturbed soil cores. *Soil Sci. Soc. Am. Proc.*, **30**, 315, 1966.
- Preman, R. R., and Garang, I. R. A gel-particle model for organic desorption from a pond sediment. *Science*, **119**, 790, 1981.
- Tremper, J. L. A natural gradient experiment on solute transport in a sand aquifer. I. Spatial moment and the advection and dispersion of conservative tracers. *Water Resour. Res.*, **20**, 675, 1984.
- Pa. J., and Leach, R. E. Aromatic compound solubility in aqueous/aqueous mixtures. *J. Environ. Eng.*, **113**, 529, 1989a.
- Pa. J., and Leach, R. E. Effect of organic solvents on sorption of aromatic organic onto soils. *J. Environ. Eng.*, **113**, 544, 1989b.
- Pohel, R., and Kuvshinov, V. Fundamental study on longitudinal dispersion of solutes in water through saturated porous media. *Water Resour. Res.*, **21**, 377, 1985.
- Porcu, T., and Smith, J. R. Field particle and intraparticle mass transport rates in aquifers. *Int. Eng. Chem. Anal.*, **13**, 187, 1973.
- Stanton, J. P., Salazar, L. B., and Smith, R. S. Large scale dispersion transport in aquifers: field experiments and reactive transport theory. *Mass. Trans. Tech. Rep.*, MIT, Eng. Report No. 315, 1988.
- Stanton, J. P., and Smith, R. S. A descriptive theory of leaching. *Soil Science*, **63**, 195, 1984.

- Goodell, J. P., Jagan, H., Packard, P., and Kinsinger, F. J. Solute transfer, with exchange between cells and stagnant water, through unexcited and fully fed rat skin. *J. Biol. Chem.*, 241, 195, 1972.
- Guillory, J. H. *Synopsis of Chromatography: Principles and Theory*. Marcel Dekker, NY, 1969.
- Guillory, J. H., and Syring, H. A molecular dynamic theory of chromatography. *J. Phys. Chem.*, 77, 448, 1973.
- Guillory, J. H., Buffing, E. A., Cherry, J. A., and Friend, E. G. An adsorption-diffusion scheme for solute transport in heterogeneous unexcited/pigged biological systems. *Water Resour. Res.*, 10, 149, 1974.
- Hendrick, R., and Goss, J. I. Theory of chromatography, Part IV: The influence of incomplete equilibration on the front boundary of chromatograms and on the effectiveness of sorption. *J. Chem. Res.*, 1972, 1972.
- Leitz, H. R. Three-dimensional analytical modeling of diffusion limited solute transport. Ph.D. Dissertation, Stanford Univ., Palo Alto, CA, 1976.
- Leitz, H. R., and Roberts, P. T. Interpreting organic solute transport. How free a field experiment using physical nonequilibrium model. *J. Great Lakes Res.*, 1, 77, 1975.
- Leitz, H. R., and Roberts, P. T. Using the method of moments to analyze three-dimensional diffusion limited solute transport. How temporal and spatial perspectives. *Water Resour. Res.*, 13, 1375, 1977.
- Leitz, H. R., and Roberts, P. T. Spatial moment simulations of physical nonequilibrium solute transport models. Application to a large-scale field experiment. *J. Great Lakes Res.*, (in press), 1979.
- Olson, R. R. Res. P. 54; and Cherry, J. A. Solute transport in aggregated cells. Tracer atom shape in relation to pore velocity distributions and adsorption. In *Free Second Symposium on Transport Processes in Porous Media*, 1973 and 1976 (Amalg. Canada), 2, 772, 1977.
- Olson, R. R., Huang, H. R., and Leitz, J. R. Transport of a reaction in a fractured well in relation to adsorption, degradation and cell cell reactions. In *The International Congress of Soil Science Transactions*, 1, 281, 1978.
- Orrock, H. E., and Roberts, J. P. Solute transport through fractured media. I. The effect of matrix diffusion. *Water Resour. Res.*, 16, 719, 1980.

- Grenier, R. Adsorption and desorption of trifluoride, trifluoride, dihalides by surface interactions. *Food Sci.*, 22, 443, 1974.
- Gross, O., Salts, J. H., Wells, P. D., and McVillie, J. B. Analysis and interpretation of single well tracer tests in unconfined aquifers. *Water Resour. Res.*, 11, 679, 1975.
- Helffer, E. Regression method in waterlogging: A further formulation using the principle of functional regression. *Statist. Sci. Technol.*, 15, 147, 1975.
- Henderson, J. E., Goring, K. A. L., and Youngson, J. Organic Matter in the Environment. Amer. Chem. Soc., Washington, D.C., 1969.
- Hessia, J. L., and Korman, J. P. Adsorption and desorption of herbicides by soils. *Weeds*, 22, 119, 1964.
- Hutchinson, L., Houghland, E. R., and Thomas, R. L. Further studies and comparative features for ion exchange columns. *Ind. Eng. Chem. Anal.*, 3, 113, 1946.
- Hypok, H., and Lendin, E. Prediction of diffusion coefficients for ion electrolytes in silica aqueous solutions. *Am. Chem. Soc. Eng. J.*, 58, 611, 1916.
- Hypok, H. R. L. Adsorption of various herbicides on soil organic matter including a short review on soil organic matter chemistry. *Soil Science Society*, 21, 131, 1976.
- Hutcherick, P. D. Ion Exchange. McGraw-Hill Book Co., 1957.
- Hutchins, R. E. The movement and desorption of fluorinated in large ions soil. *Ph. D. Dissertation*, Williams in Univ., 1979.
- Hutchins, R. E., Hutchins, J. E., Clifton, J. E., and Johnson, A. E. Transport of organic compounds with saturated groundwater flow. *Experimental results*. *Water Resour. Res.*, 12, 275, 1976.
- Inamdar, P. J., and Pytko, J. B. Groundwater sorption of phenolic compounds by confined flowlines: the role of confined organic matter. *Environ. Sci. Technol.*, 18, 62, 1984.
- Irwin, G. P. A derivation of the particle size weighting factor in the measurement of mass coefficients. *Chem. Eng. Sci.*, 14, 693, 1959.
- Jacob, T. E., and Peters, E. L. Desorption kinetics in modeling of toxic chemicals. *J. Env. Eng. Div. ASCE*, 109, 439, 1983.
- Jacobson, P. E., Wilson, E. T., and Johnson, R. J. Modeling the transport of herbicide ions through unflooded soil columns from two contrasting watersheds. *Soil Sci. Soc. Am. J.*, 52, 1152, 1988.

- Jennings, A.R., and Kirwan, R.J. Desferrioxamine upgliding: optimization analysis. *J. Hydraul. Eng.*, 108, 1998, 1994.
- Jury, E.A. Simulation of solute transport using a transfer function model. *Water Resour. Res.*, 11, 541, 1975.
- Jury, E.A., Hsieh, H., and Roberts, R. Field study of macropore movement through unsaturated soil. *Water Resour. Res.*, 21, 749, 1985.
- Jury, E.A., Speite, S., and White, R.E. A transfer function model of solute transport through soil 1. Fundamental concepts. *Water Resour. Res.*, 22, 145, 1986.
- Karickhoff, H.W. Sorption kinetics of hydrophobic pollutants in natural sediments. In: *Contaminants and Sediments*, Baker, R. A., [ed.], Vol. 1, Ann Arbor Science Publ., Ann Arbor, MI, 1982.
- Karickhoff, H.W. Semi-empirical verification of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere*, 10, 833, 1981.
- Karickhoff, H.W. Organic pollutant sorption in aquatic systems. *J. Hydrol. Eng.*, 100, 740, 1984.
- Karickhoff, H.W., Brown, D.E., and Scott, P.A. Sorption of hydrophobic organic chemicals by sediments. *Water Res.*, 17, 361, 1983.
- Karickhoff, H.W., and Bartha, R.B. Sorption dynamics of hydrophobic pollutants by sediment suspensions. *Environ. Tox. Chem.*, 4, 145, 1985.
- Katzen, F.R., Lapinski, L., and Anderson, W.R. Mechanisms of adsorption in soils. 5. Effects of intraparticle diffusion in flow systems in fused beds. *J. Phys. Chem.*, 74, 493, 1970.
- Kennedy, E.R., and Caring, C.A.T. Relationship between water solubility, soil sorption, octanol-water partitioning, and concentration of chemicals in biota. In: *Aquatic Toxicology*, Am. Soc. Test Mater. Philadelphia, Pa., 1980.
- Kay, E.D., and Glavin, R.E. Adsorption and movement of lindane in soils. *Soil Sci. Soc. Am.*, 29, 594, 1967.
- Khan, S.U. Influence and kinetic modeling of the adsorption of D.D.T and polycyclic aromatic acids. *Can. J. Soil Sci.*, 55, 629, 1975.
- Khan, S.U. Adsorption of D.D.T from aqueous solution by kaolite acid-clay complex. *Environ. Sci. Technol.*, 8, 126, 1974.
- Khan, S.U. The interactions of organic matter with pesticides. In: *Soil Organic Matter*, Khakhria, S., and Khan, S.U. [eds.], Elsevier Publ. Co. 1974.

- Ross, J. H., and Helmer, L. A new gas chromatographic method for measuring porous diffusion coefficients and determining factors and sizes. *J. Polym. Sci.*, **54**, 1477, 1962.
- Seitman, E. R. E., and Hitchman, J. G. Cation exchange with a synthetic phenolsulfonate resin. *Analyst Soc. Chem.*, **7**, 90, 1960.
- Stupp, E. R., and Ulrich, E. E. Methyl displacement in an unsaturated glass bead matrix. *Anal. Chem.*, **36**, 489, 1964.
- Stuart, E. Contribution to the theory of chromatography: Linear and equilibrium column chromatography. *J. Chromat.*, **19**, 277, 1962.
- Stuart, E., and Stupp, E. E. Series of column exchange in ion-exchange resins. *J. Phys. Coll. Chem.*, **66**, 1113, 1962.
- LaPlante, E. E. Sorption of sorbates by metal oxide and aqueous oxide resin and equilibria. *Anal. Chem.*, **49**, 84, 1977a.
- LaPlante, E. E. Sorption of sorbates by metal oxide and aqueous oxide resin and equilibria. *Anal. Chem.*, **49**, 117, 84, 1977b.
- LaPlante, E. E., McLaughlin, W. E., and Stupp, E. E. Trifluoromethane persistence in ion-exchange resin. *Anal. Chem.*, **49**, 128, 115, 1977c.
- Leptin, L., and Jacobson, E. E. Mathematics of absorption in beds. VI. The effects of longitudinal diffusion in ion exchange and chromatographic systems. *J. Phys. Chem.*, **66**, 154, 1962.
- Leary, E. E. Multidimensional column transport incorporating equilibrium and rate limited phenomena with first-order loss. XI. An approximate simulation of a column input. *Water Resour. Res.*, **10**, 111, 1974.
- Levy, J. E., Gilbert, J. E., and Burlington. On the amount and composition of the size and density values collected at Richmond. *William Leary and Sons, London*, 1942.
- Lee, L. E. The influence of solvent and surface characteristics of the distribution of porous-spherical. M. S. Thesis, University of Florida, Gainesville, 1969.
- Lee, L. E., Lee, F. E. C., Brumby, E. J., and Ogden, E. E. Non-equilibrium sorption of organic contaminants during flow through columns of solid sorbents. *Env. Toxicol. Chem.*, **7**, 179, 1988.
- Lee, L. E., Lee, F. E. C., and Shieh, H. P. The influence of solvent characteristics on the sorption and distribution of porous-spherical. *Agencies Abstracts Amer. Soc. Agenc. Resour. Sci.*, 1988.

- Landon, J. A., and Atkinson, J. L. A kinetic and equilibrium study of the adsorption of carbonyl and parathion upon soil organic matter residues. *Soil Sci. Soc. Am. Proc.*, 35, 758, 1971.
- Lauer, R. A., Broadway, R. R., and Pennington, T. J. The effect of acid and potential on nickel anion diffusion. *J. Hydrol.*, 18, 44, 1961.
- Li, S., and Follis, S. S. A study of the mechanism of cationic adsorption by humic acid from weak soil. *Soil Sci.*, 113, 143, 1971.
- Lindstrom, P. T., and Brinson, L. A theory on the mass transport of previously distributed chemicals in a water saturated sorbing porous medium. *Soil Sci.*, 111, 191, 1971.
- Lyman, W. J., Reehl, W. F., and Bunche, G. R. *Handbook of Chemical Property Estimation Methods*. McGraw-Hill Book Co., New York, NY, 1969.
- Meekap, S. S., Proberg, S. L., Roberts, P. V., and Cherry, J. A. A natural gradient experiment on solute transport in a sand aquifer. I. Approach and overview of phase concept. *Water Resour. Res.*, 21, 2611, 1985a.
- Meekap, S. S., Hall, W. F., and Roberts, P. V. Variability of sorption properties in a field experiment on groundwater transport of organic solutes. *J. Cont. Hydrol.*, 3, 119, 1985b.
- Mezall, P. J., and Agin, P. L. Adsorption kinetics of plume as affected by residual mass in the soil. *Env. Tox. Chem.*, 4, 17, 1985.
- McClintock, W. B., and Boyer, T. R. Thermodynamics of fluoride adsorption and desorption on three California soils. *Soil Sci. Soc. Am. J.* 35, 495, 1971.
- McCre, S. J., and Ruffin, A. J. Adsorbed film chromatographic measurement of gaseous diffusion coefficients. *Chem. Eng. Commun.*, 11, 219, 1984.
- Meier, S., Griesbach, R. J., and Agin, P. L. Two resistance mass transport model for the adsorption of urea on Fuller's earth. *Water Air Soil Poll.*, 11, 129, 1982.
- Meister, R. A., and Wolfe, J. P. NONLIN nonlinear least squares fitting and function minimization. Supplementary Program No. 38 FORTRAN Version Computing Center, Madison, WI, 1981.
- Mezall, P. J., Meier, P. J., and Johnson, P. L. High-level waste glass field burial tests at WIPP. The effects of groundwater flow on the release and migration of fluoride from a sandy matrix. *Atomic Energy Canada Ltd.*, 1985.

- Miller, E.T., and Nelson, W.J. Sorption of hydrophobic organic pollutants in aggregated soil systems. *J. Environ. Hydraul.*, 1, 261, 1986.
- Schaefer, A. B., and Hansen, S. Theoretical prediction of sorption curves for molecular solutes. *Chem. Eng. Sci.*, 16, 1439, 1969.
- Schaefer, A.B., Hansen, S., and Jacob, B.B. Effect of adsorbed particles size distribution on Washburn-type curves for molecular solute columns. *Chem. Eng. Sci.*, 11, 1791, 1966.
- Sells, P.J., Goren, S., and McVittie, J.G. An examination of scale-dependent dispersion coefficients. *Ground Water*, 11, 703, 1973.
- Sells, P.J., Goren, S., McVittie, J.G., and Greenberg, R.B. Performance, analysis, and simulation of a two well tracer test at the Mobile site. *Water Resour. Res.*, 18, 1803, 1982.
- Sells, P.J., Goren, S., McVittie, J.G., Edwards, J.B., and Greenhalgh, J.B. Permeability gradient tracer tests and inferred hydrologic conductivity distributions at the Mobile site. *Ground Water*, 26, 109, 1988.
- Sposito, G., and Van Kesteren, J. Soil leachability of herbicide derived aniline residues--A thermodynamic approach. *Soil Sci.*, 117, 1, 1977.
- Suzukawa, I., Kurihara, K., Sanoaka, T., and Iwano, T. Desorption of solute transport in unsaturated soil system by initial component flow model. *Proc. Environ. Toxicol. Hyg. Res.*, 10, 9, 1986 (in Japanese).
- Wettli, E.H., Hengstenberg, E., Hinz, E., Gessle, P., and Yellandby, L.B. Solubility of aromatic pollutants in aliphatic solvents. *Chemosphere*, 12, 115, 1983.
- Weyer, J.B., Schaeffer, B.B., and Hansen, S.B. Desorption of some herbicides from nonuniformly sized and aged soil. *Can. J. Soil Sci.*, 51, 429, 1970.
- Wetzel, S., and Sylvestre, L.B.B. On flow coefficient and adsorption dynamics during scale transport in soils. *Nature* 195, 417, 1966.
- Wongpan, S.B. Adsorption of picolene by humic acids and humin. *Soil Sci.*, 126, 370, 1969.
- Wong, Sheng, P., Higgs, J.B., Wells, B.B., van Doren, S.B., Viallegas, P.J., Davidson, J.W., and Wilson, S.B. On the applications of two conceptual models for describing the exchange during transport through an aggregated soil. *Water Resour. Res.*, 20, 1113, 1984.

- Reed-Kline, F., Brownson, G.L., Rao, P.D.C., and Bernick, A.B. Desorbtion of vapors during displacement of hydrophobic organic chemicals and ^{60}Co through soil columns with organic and mixed solvents. *Environ. Sci. Technol.*, 15, 1281, 1981.
- Reed-Kline, F., Rao, P.D.C., and Bernick, A.B. Collection of organic sorbents on sorption of hydrophobic organic chemicals by soils. *Environ. Sci. Technol.*, 15, 513, 1981.
- Reed-Kline, F., Rao, P.D.C., and Bernick, A.B. The influence of organic sorbents on leaching of hydrophobic organic chemicals through soils. *Environ. Sci. Technol.*, 15, 1287, 1981.
- Reed-Kline, F., Rao, P.D.C., Jernay, R.E., and Fickman, J.H. Ion exchange and diffusion mass transfer during chemical displacement through an aggregated soil. *Soil Sci. Soc. Am.*, 46, 431, 1982.
- O'Donner, E.A., and Anderson, J.B. Soil factors affecting the adsorption of 1,4-D-T. *Soil Sci. Soc. Am. Proc.*, 38, 445, 1974.
- Odum, J.E., Lacey, J., and Wicks, L.V. Sorbed distribution of organic chemicals in solution and adsorbed as a function of position and time for various chemical and soil properties. *Soil Sci. Soc. Am. Trans.*, 34, 418, 1970.
- Oliver, E.B. Desorption of chlorinated hydrocarbons from soil and nonaqueous-phase contaminated sediments. *Chemosphere*, 14, 1047, 1985.
- Rank, L., Radek, J.B., and Bailey, S.J. Incompressible diffusion coefficients in packed column. Measurement by constant-flow gas chromatography. *Am. Instit. Chem. Eng. J.*, 19, 710, 1987.
- Parker, J.C., and Valocchi, A.J. Considerations on the validity of equilibrium and first-order kinetic transport models in structured soils. *Water Resour. Res.*, 20, 389, 1984.
- Petersen, J.E. Hydrodynamic dispersion in aggregated soils I. Theory. *Soil Sci. Soc. J.*, 33, 119, 1969.
- Petersen, J.E., and Rao, S.S. Hydrodynamic dispersion in aggregated soils II. Effects of velocity and aggregate size. *Soil Science Soc. J.*, 34, 291, 1970.
- Petersen, J.E., and Lickhiser, H.B. Laboratory simulation of pertrichloroethene behavior in an adjacent aquifer. *Water Resour. J. Canada*, 20, 647, 1987.
- Pillay, S.S. Longitudinal dispersion from parabolic diffusion, and liquid phase mass transfer during flow through soil-particle systems. *Trans. Am. Soc. Civ. Eng.*, 74, 1962.

- Flaherty, J. F., and Schenk, K.E. Solute-dependent dispersion in a stratified granular medium. *Water Resour. Res.*, 17, 1181, 1981.
- Flaherty, J. F., Johnson, R. E., Turk, R. J., and Moritt, W. P. Measurement of distribution coefficients using a radial injection dual-tracer test. *Water Resour. Res.*, 17, 1219, 1981.
- Haras, P. & G. Transport in structured porous media. In: *Flow and Transport in Porous Media*, Velasco, L., and Haras, P. (Eds.), John Wiley & Sons, New York, 1981.
- Hesse, P. R. C. Tracing patterns of water and solutes in unsaturated zones. In: *Advances in Porous Media*, Toran, E., Ng, C., and Goldschmidt, I. (eds.), 1986.
- Kapoor, R. L., and Anderson, R. M. Simulation of chromatographic response in columns packed with N-dipole oriented particles. *Chem. Eng. Sci.*, 45, 199, 1990.
- Kee, P. R. C., Davidson, J. B., Jassby, R. E., and Bell, R. M. Evaluation of conceptual models for describing nonequilibrium adsorption-desorption of pesticides during co-sorption in soils. *Soil Sci. Soc. Am. J.*, 45, 115, 1981.
- Kee, P. R. C., Green, R. E., Gupta, L. R., and Davidson, J. B. Evaluation of a capillary bundle model for describing solute dispersion in aggregated soils. *Soil Sci. Soc. Am. J.*, 49, 415, 1985.
- Kee, P. R. C., Green, R. E., Schindlerbaum, T., and Renshaw, T. Field study of solute movement in a highly aggregated soil with intermediate clumping. In: *Advances in Porous Media*, J. Toran, 1986.
- Kee, P. R. C., Knappe, A. J., Kapoor, R. E., and Muel, K. L. Sorption and transport of hydrophobic organic chemicals in aqueous and mixed solvent systems: Model development and preliminary evaluation. *Environ. Qual.*, 14, 179, 1984.
- Kee, P. R. C., and Jassby, R. E. Sorption and movement of pesticides and other toxic organic substances in soils. In: *Chemical Mobility and Reactivity in Soil Systems*, ASA, SSSA, 1982.
- Kee, P. R. C., Jassby, R. E., and Anderson, R. M. Experimental and theoretical aspects of solute diffusion in spherical and non-spherical aggregates. *Soil Sci. Soc. Am. J.*, 48, 1981.
- Kee, P. R. C., Jassby, R. E., Bell, R. M., Davidson, J. B., and Renshaw, T. P. Experimental and mathematical description of nonequilibrium solute transfer by diffusion in spherical aggregates. *Soil Sci. Soc. Am. J.*, 44, 446, 1980.

- Lee, P. H. E., and Lee, L. T. Sorption of organic chemicals by soils from solid solvent and multicomponent mixtures. pp 437-451. In Proc. 10th Stanford Life Sci Symp., 1980 Symp. Series 83, Redwood P&L, Richmond, Va, 1987.
- Lee, P. H. E.; Bellman, R. E.; Jorgens, D. E., and Savitsky, J. H. Solute transport in aggregated porous media. Theoretical and experimental evaluation. Soil Sci Soc Am J., 46, 1477, 1982.
- Levenson, A. Transport phenomena and mechanisms in an isothermal fixed-bed catalytic reactor. Chem. Eng. Sci., 37, 421, 1982.
- Levenson, A. The influence of particle shape on the dynamics of fixed beds. Chem. Eng. Sci., 46, 1479, 1983a.
- Levenson, A. The effect of particles of variable size, shape, and properties on the dynamics of fixed beds. Chem. Eng. Sci., 48, 441, 1983b.
- Liberman, P. C.; Chinn, H. H., and Mackay, G. H. A natural gradient experiment on solute transport in a sand aquifer. III. Saturation evolution and mass balance for organic vapors. Water Resour. Res., 21, 1663, 1985.
- Liberman, P. C.; Chinn, H. H.; Rogers, R. E.; Critchfield, J. H., and Smith-Ryan, P. The influence of mass transfer on solute transport in column experiments with an aggregated soil. J. Colloid Interface Sci., 1, 279, 1987.
- Liberman, P. C.; Mackay, P. L.; Liberman, H., and Liberman, J. Organic contaminant inhibition during groundwater recharge. J. Water Poll. Control Fed., 51, 103, 1988.
- Lyons, C. E. Formation of gases and vapors in polymers. In Polymer Permeability Groups. J. Vol 5 Elsevier, London, England, Chapter 1, 1982.
- Meun, J. L. Kinetics of a fixed bed system for solid diffusion into spherical particles. J. Chem. Phys., 30, 347, 1958.
- Miller, J. P.; Wilkowsky, R. E. Transient and deviations from log linear behavior. Pharm. Res., 4, 221, 1987.
- Miller, G. H. Principles of Adsorption and Adsorption Processes. Wiley Interscience, NY, 1966.
- Miller, G. H., and Langhin, R. P. The effect of crystallite shape and size distribution on diffusion environments in molecular sieves. Chem. Eng. Sci., 16, 471, 1960.
- Salije, A. In the prediction of soil sorption coefficients of organic pesticides from molecular structure: applications of a molecular modeling model. Environ. Sci. Technol., 21, 158, 1987.

- Wittem, F., Hilgen, L., and Thren, G. Adsorption-desorption of parabens as affected by soil organic matter. *J. Agric. Food Chem.*, 30, 1224, 1982.
- Schulze, R. *Radioisotomen, Chemie und Biologie*. In: *Soil Organic Matter*, Schulze, R., and Thren, G. V. (eds.), Elsevier Publ., NY, 1981.
- Schmiedel, E. *Die Physik des Bodens*. Berlin, Germany, 1959.
- Schwenenbach, R. P., and Russell, J. Transport of sorptive organic compounds from surface water to groundwater: Laboratory sorption studies. *Environ. Sci. Technol.*, 15, 1268, 1981.
- Sellin, R. H., Swenson, J. R., and Russell, R. H. Evaluation of a two site adsorption-desorption model for dissolving solute transport in soils. *Proc. Super-Superfund Studies Conf.*, Wash. D.C., 1984.
- Seyfried, R. E., and Rao, P. E. Solute transport in undisturbed columns of an aggregated tropical soil. *Hydrological flow effects*. *Soil Sci. Soc. Am. J.*, 54, 1034, 1990.
- Shaw, J. *Correlation analysis in organic chemistry: An introduction*. Pt. Linear Free-energy Relationship. Clarendon Press, Oxford, England, 1973.
- Hagen, J. J., Frickham, A. E., and Tuck, L. R. Diffusion characteristics of 1,3 Dichloropropane and 1,2 Dichloroethane in soils. *Soil Sci. Soc. J.*, 55, 101, 1991.
- Hogg, J., and Havelok, A. E. Two phase model for the sorption displacement of reactive solutes in soils. *Soil Sci. Soc. Am. J.*, 58, 243, 1994.
- Hatch, L., and Schwab, P. W. Mass transport I: Analysis of uncertainty in prediction. *Water Resour. Res.*, 27, 211, 1991.
- Hawthornth, G. E. Movement of water-soluble metal cations through a forest soil column. *Environ. Toxicol.*, 12, 277, 1987.
- Hawthornth, G. E., Weyer, R. W., and Kallan, J. L. Comparison of models that describe the transport of organic compounds in macroporous soil. *Environ. Toxicol. Chem.*, 4, 251, 1987.
- Havlik, T., and Dougherty, B. E. Effects of spatially varying adsorption properties on contaminant transport in saturated porous soils. *Trans. Am. Society Civil En.*, 198, 1987.
- Himelvi, P. Haplo diffusion. In: *Diffusion in Polymers* (Huggert, E. Grah. J., and Puck, G. G. (eds.) Academic Press, London, 1969.

- ROBERT, R. O., PUGHMAN, R. W., and KELLEY, E. A. Experimental investigation of solute transport in fractured porous media. 2. The reactive case. *Water Resour. Res.*, **21**, 1263, 1985.
- ROBERT, E. A. A natural gradient experiment on solute transport in a sand aquifer: Spatial variability of hydraulic conductivity and its role in the dispersion process. *Water Resour. Res.*, **22**, 2909, 1986.
- ROBERT, E. A. The Laplace Transform-Chebyshev technique: A time-continuous finite element theory and application to mass transport in groundwater. *Water Resour. Res.* (in press), 1989.
- ROBERTSON, J. R., and TOLSON, H. T. A study of the interaction of E. coli bacteria with sand media from three different wells. *Soil Science*, **52B**, 62, 1946.
- TOLENT, A. J. Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils. *Water Resour. Res.*, **21**, 499, 1985.
- TOLENT, A. J. Theoretical analysis of deviations from local equilibrium during sorbing solute transport through idealized stratified profiles. *J. Geosci. Spectr.*, **3**, 181, 1988.
- VAN DERMEEREN, H. Th. Non equilibrium transport parameters from chloride displacement experiments. I.R. Institute for W & E. Report Agricultural Research Report No. 118, 1980.
- VAN DERMEEREN, H. Th. A general approach for modeling solute transport in structured soils. In *Proc. Hydrogeology of Soils of low Hydraulic Conductivity* (Meeting of the IAB, Vol. 17, Part I, 313, 1982).
- VAN DERMEEREN, H. Th., BOUTHEUX, P. R., and KLEINGA, P. J. An evaluation of kinetic and equilibrium equations for the prediction of pesticide movement through porous media. *Soil Sci. Soc. Am. Soc.*, **48**, 12, 1276.
- VAN DERMEEREN, H. Th., and PARKER, J. C. Boundary conditions for displacement experiments through short laboratory soil columns. *Soil Sci. Soc. Am. J.*, **48**, 783, 1984.
- VAN DERMEEREN, H. Th., and KLEINGA, P. J. Mass transfer studies in sorbing porous media. Analytical solutions. *Soil Sci. Soc. Am. J.*, **48**, 873, 1984.
- VAN DERMEEREN, H. Th., and KLEINGA, P. J. Mass transfer studies in sorbing porous media. Experimental evaluation with TUDOR (Nag). *Soil Sci. Soc. Am. J.*, **48**, 1278, 1984.

- van Genuchten, M Th., Wieringa, P J., and O'Leary, M A. Mass transfer system for arctic permafrost soils: Experimental evaluation with L.A.S.-L. Soil Sci. Soc. Am. J., 44, 179, 1979.
- van Genuchten, M Th., Topp, W C., and Chaudhary, R. Mass water soluteless soil solute transport through soils containing large cylindrical macropores. Water Resour. Res., 20, 221, 1984.
- Vanhook, E. Handbook of environmental data on organic chemicals, 2nd ed. Van Nostrand Reinhold Co., NY, 1965.
- Villerman, J. Reformation of chromatographic peaks under the influence of mass transfer phenomena. J. Chromatogr., 12, 312, 1954.
- Wilcox, R F., and Salasgui-Elia, A. Sorption of 1,1,2,2-tetrachloroethane & hexane to soils from water-saturated mixtures. Environ. Sci. Technol., 11, 312, 1977.
- Wilcox, R F., and Lin, R F. Determination of mass transport parameters for fluid-bed adsorbents. Chem. Eng. Commun., 1, 30, 1978.
- Wilcox, R F., and Norling, J B. Kinetics of adsorption on carbon from solution. J. Nuclear Energy, B2C - Div. Am. Nucl. Civil Eng., 1, 302, 1963.
- Wilcox, R F. A new model for toxic materials and their interactions with hydrophobic organic chemicals in soil water systems. J. Canadian. J. Hydrol., 1, 28, 1985.
- Wills, R E. The influence of macropores on the transport of dissolved and suspended matter through soil. In: Soil Sci. Soc. Trans., 84, 1, 1961, Springer Verlag 85-1, 83, 1963.
- Wills, R E. Ryan, J B.; Givoli, E. and Topp, W. Loading of sorptolites through water-filled pores of a saturated clay soil. Soil Sci. Soc. Am. Proc., 30, 221, 1966.
- Wills, R. and Rablitz, I A. The experimental loading pattern of nitrate and chloride in a loamy sand under field conditions. J. Soil Sci., 27, 440, 1974.
- Wilson, J B. A theory of chromatography. J. Am. Chem. Soc., 44, 1943, 1946.
- Wood, E L.; Reinhard, D C.; and Lee, P H C. Influence of solution composition on the sorption and transport of organic solutes against electric fields. Amer. Soc. Agric. Mech., 61, 1971.
- Working: C E. The Florida Manual. Seventh edition. Florida Crop Protection Council. Louisiana Press. Tallahassee, Florida 1981.

- Wu, S., and Gekkerud, P. B. Sorption kinetics of hydrophobic organic compounds to natural sediments and soils. *Environ. Sci. Technol.*, 20, 721, 1986.
- Yakovlevy, S. B., Flynn, H. L., and Andrus, G. G. Solubility of nonelectrolytes in polar solvents. *J. Pharm. Sci.*, 41, 881, 1952.
- Yakovlevy, S. B., and Berman, I. Solubility in Tetrahydrofuran of Substitution of Drugs. *Yakovlevy, S. B. (ed.) Annual Review*, 89, 1982.
- Zeprevski, J. B., Fourn, S. B. and Hase, J. B. The kinetics of adsorption of phenols by granular activated carbon. *J. Coll. Inter. Sci.*, 20, 178, 1966.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate in scope and quality, as a dissertation for the degree of Master of Philosophy


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August, 1909



Dean, Graduate School

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